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Assesment of Ammonia Volatility from Fall Surface-Applied Liquid Dairy Manure

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ASSESSMENT OF AMMONIA VOLATILITY FROM FALL SURFACE-APPLIED LIQUID DAIRY MANURE

A Thesis Presented

by

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ABSTRACT

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Ammonia emissions from dairy and livestock operations are of significant environmental and human health concern in the United States. Conservation of ammonia from fall surface-applied manure could benefit farmers by retaining nitrogen for use by crops in the spring growing season. The primary goal of this research was to investigate a management strategy for mitigating ammonia volatility from cow manure at the time of field application with no incorporation in the fall before snow fall. The hypothesis is that application of manure in cooler fall temperatures will slow the rate of ammonia volatilization. The objective was achieved by studying the effect of temperature on ammonia volatility from surface-applied liquid dairy manure applied every month over a period of four months from September to December, 2008. Manure was surface-applied to a field cover cropped with winter rye (*Secale cereale* L.) on September 15th. Ammonia emissions were measured using a dynamic chamber method. Results showed ammonia losses in December were approximately one fifth of the losses encountered in September.

Colder temperatures significantly reduced rates of volatility and amounts of nitrate found in the soil. However, N-accumulation in the cover crop fluctuated and was not significantly different from month to month. The greatest nitrogen retention and lowest rates of ammonia volatility came from manure applied to frozen ground in December. Surface application of liquid dairy manure should be conducted as late as possible in the fall before snow fall for the least amount of nitrogen lost to ammonia volatilization. Planting a cover crop at the time of fall harvest in conjunction with a late fall (November or December) manure application is a nutrient management strategy which deserves further investigation.

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CHAPTER I

LITERATURE REVIEW

Introduction

Ammonia emissions from dairy and livestock operations are of significant environmental and human health concern in the United States and around the globe. Ammonia volatility from manure varies widely depending on species of animal, its diet and housing, manure storing and handling, technique of land application of the manure, and ambient conditions. The focus of this review will be to explore the causes of ammonia volatility from the liquid manure of dairy cows and current methods of mitigation as this is the highest source of ammonia emissions in the state of Massachusetts (EPA, 2005) where this research project was conducted.

Manure is a combination of urine and feces. Nitrogen content of dairy manure consists of approximately 50% inorganic N in the form of ammonia and 50% organic nitrogen at the time of surface application to agricultural fields (Jokela and Meisinger, 2008). If the ammonia volatilizes, only one half of the total available nitrogen is left in the organic form which takes much longer to decompose. Many studies have indicated that up to 90% of the ammoniacal nitrogen found in manure can volatilize within the first day of application if not injected or incorporated into the soil immediately (Stevens and Laughlin, 1997; Meisinger and Jokela, 2000; Huigsmans, 2003). Need for improved manure management by dairy farmers becomes increasingly apparent as fertilizer costs continue to rise and environmental degradation continues to occur due to atmospheric nitrogen deposition and eutrophication of waterways.

In order to properly mitigate ammonia volatility from animal manure, it is imperative to first understand how nitrogen is excreted in manure. Nitrogen is excreted largely as urea in livestock urine, and also as urea, ammonia, and mostly organic nitrogen in livestock feces. The urease enzyme is produced by several microbe species present in feces and soil that convert urea to ammonia rapidly once excreted. This typically occurs in a matter of hours if environmental conditions are favorable, although mineralization may continue for several months while the manure is in storage. Urea is hydrolyzed by the urease enzyme as follows:

$$CO(NH_2)_2 + 2H_2O \rightarrow (NH_4)_2CO_3 \rightleftarrows 2NH_4^+ + CO_3^{2-}$$

(Bussink and Oenema, 1998)

The formation and dissociation of ammonium carbonate $(NH_4)_2CO_3$ causes urea to have a high ammonia (NH_3) volatilization potential. Organic nitrogen on the other hand requires months or even years to mineralize through microbial decomposition and ammonification (Gay and Knowlton, 2005).

This literature review gives an overview of the essential areas of information required to thoroughly understand and effectively mitigate ammonia emissions. A global perspective of ammonia emissions describes the current status of ammonia mitigation worldwide and discusses national and international regulations that have been implemented to address the problem. The current state of dairy production and manure management in the state of Massachusetts is also discussed in this section. Next, the many mitigation techniques that have been researched and implemented are discussed and compared for their general effectiveness. Following a discussion of mitigation techniques is an overview of research into select environmental factors affecting ammonia volatility that must be thoroughly understood in order to improve mitigation techniques. Finally, the many methods of measuring ammonia emissions that have been developed is discussed. It is apparent that without a globally or even nationally accepted standard set of methods, experimental results of ammonia emissions cannot be compared, and ultimately an agreement on "best management practices" cannot be reached.

Ammonia Volatility Worldwide

Anthropogenic production of reactive nitrogen, particularly from agricultural activities in the last few decades, now exceeds natural fixation of nitrogen (N_2) (Galloway, 2004). According to a recent ammonia emission assessment of agriculture in the United States, accumulation of atmospheric nitrogen enhances the scope of the global nitrogen cycle contributing to the following environmental consequences: "acidification and eutrophication, photochemical air pollution, reduced visibility, ecosystem fertilization, global warming, and stratospheric ozone depletion" (Aneja et al., 2008). Ammonia-based photochemical air pollution forms particulate matter ($PM_{2.5}$) that is of great environmental and health concern. "$PM_{2.5}$ refers to all particulate matter suspended in the ambient air which is less than or equal to 2.5 μm in aerodynamic diameter" (Martin et al., 2008). Ammonia gas is a precursor of photochemical air pollution, which is to say that it forms secondary particulate matter ($PM_{2.5}$) with sulfides to create other pollutants harmful to human and animal health. Inhalation of $PM_{2.5}$ affects lung tissue and increases the risk of lung cancer. Ammonium sulfate and ammonium nitrate are two types of $PM_{2.5}$ formed by volatilized ammonia (Martin et al., 2008).

Galloway et al. (2004), in their review of the global nitrogen cycle over the last century, estimated that Asia, Europe, and North America were producing 90% of the global NH_3 emissions in the early 1990s, with Asia producing the largest portion of atmospheric NH_3 (22.1 Tg $N.yr^{-1}$). However, little research on ammonia volatility has been conducted in this region of the world. Despite the global concern, global ammonia emission estimates are inaccurate due to the lack of experimental data and lack of continuity between methods of measurement. Only a few European and North American countries have a history of monitoring ammonia emissions from agricultural sources. In the early 1990s, up to 90% of atmospheric ammonia in Europe was linked to agriculture, especially its use of dairy cattle manure (Asman, 1992, and ECETOC, 1994). With an increase of chemical fertilizer use in the 1950s after World War II, farm manure became less important as an on-farm source of soil fertility, and eventually became a source of environmental pollution. In combination with increases in chemical fertilizer use, number of animals, and dietary N content, NH_3 emissions also increased by about 50% between 1950 and 1980 (Apsimon et al., 1987). In an effort to reduce ammonia emissions, the European Union signed the convention on *Good Agricultural Practice for Reducing Ammonia* (2001) proposed by the UN Convention on Long-range Transboundry Air Pollution (CLRTAP). Results from enforcement of this convention are beginning to be seen. The United Kingdom's National Atmospheric Emissions Inventory has stated that:

> Emissions in 2006 represent a decrease of 18% on the 1990 emissions. The primary source of NH_3 emissions in the UK is manure management from livestock, and in particular cattle. The most significant cause of reductions in recent years has been decreasing cattle numbers in the UK. (http://www.naei.org.uk/pollutantdetail.php)

According to one recent global estimate reported by Beusen et al. (2008), total global agricultural ammonia emissions range from 27–38 (with a mean of 32) Tg NH_3-N

yr^{-1}, with livestock production contributing from 16–27 (with a mean of 21) Tg NH_3-N yr^{-1}. Emissions from livestock production are categorized as 31–55% coming from animal housing and manure storage, 17–37% from grazing animals, and 23–38% from land application of manure. This indicates that global reductions are still imperative.

In a previous study, the "Inventory of Ammonia Emissions from UK Agriculture" (2004) estimated that more than one half of all emissions came from cattle manure based on animal type and a quarter of all emissions came from land application based on methods of manure management. Several European nations have done extensive research in the area of ammonia volatility from animal production, and farmers in the Netherlands are required to apply manure to their fields using ammonia reduction techniques (Webb et al., 2005), some of which will be discussed in the section on the mitigation of ammonia volatility.

New laws regulating ammonia emissions from animal operations in the United States were passed in January 2009 (http://www.extension.org), but are not as stringent as European regulations for reducing ammonia emissions. Under the new laws, only Concentrated Animal Feeding Operations (CAFOs) that own more than 750 cows must report emission estimates, and rather than being required to practice ammonia reduction techniques, they are required to pay a fine of $25,000 per day for not complying with the new rules that prohibit emissions above 100 lbs. NH_3 per day (Henry and Stowell, 2009). Research is still lacking in all regions of the United States with animal operations, and experiments to measure significant changes in volatility due to seasonal effects often do not cover a significant period of time (Aneja et al., 2008). There is very little information about ammonia volatility from dairy and livestock operations in Massachusetts, particularly in regard to seasonal changes.

In 2005, the United States Environmental Protection Agency's (EPA) national estimates for ammonia volatility from dairy and beef cattle alone accounted for about one half of total ammonia emissions from animal wastes. In Massachusetts that year, dairy farms were responsible for 1,092 tons of NH_3 while all other animal operations were responsible for only an estimated 615 tons of NH_3/yr (EPA). Furthermore, in the United States, most ammonia loss from manure occurs at the time of land application. This indicates that manure is poorly managed nationwide, and that in Massachusetts dairy farms in particular are prime subjects for improvements in manure management. According to a nutrient management survey of dairy farms in Massachusetts conducted by the University of Massachusetts Extension in 2006, most dairy farmers did not have a manure management plan, but were interested in developing one (Herbert et al., 2007).

Most Massachusetts dairy farms are small in scale–200 milking cows or fewer– and therefore are not required to comply with the new EPA regulations however they still emit a significant amount of ammonia annually. These farms typically have only enough manure storage capacity for six months, meaning they must empty the storage container twice a year. Besides the limited infrastructure, farmers are also limited by inadequate time and machinery to manage or spread manure properly throughout the year. Although immediate disking or injecting manure into the soil is considered one of the best management methods for manure application, most farmers do not have the machinery needed to complete the job in one pass over a field, and do not have time to return and disk manure into the soil. Hay fields, pasture, and no-till planted corn fields are other areas that farmers may need to fertilize with manure, but where they are also unable to incorporate manure into the soil. Research on low cost ammonia mitigation techniques for small-scale dairy farms in Massachusetts is needed.

Manure Management for Mitigation of Ammonia Volatility

From a whole farm system perspective, manure must be managed to reduce a wide range of pollutants while maintaining soil fertility. Conservation of nutrients from manure allows a farm to be more self sustaining by reducing the need for external inputs such as costly chemical fertilizers which improves the whole farm nutrient cycling system. Manure has been used as a fertility source for crops for centuries. Research in methods of nitrogen conservation from manure is over a century old. Recommendations for manure additives and incorporation of manure with the soil were first made in the early 1900s. (Heck, 1931). However, many of these conservation methods were not implemented a century ago due to their high financial and labor cost; the same reasons for not practicing better manure management are true today.

An important consideration related to the practicality of the many techniques for mitigating ammonia volatility are the economic costs associated with them. Guides such as the Air Management Practices Assessment Tool designed by Iowa State University (http://www.extension.iastate.edu/airquality) provide a conservative estimate of the range in effectiveness and relative cost for many mitigation methods. Further assurance that methods of ammonia mitigation will be implemented comes from national laws, regulations, and incentive programs for animal producers. Manure composting, production of methane biogas for energy, and value added products such as CowPots (http://www.cowpots.com) are other applications for manure conservation that can be profitable to the farmer.

Many aspects of animal production are susceptible to ammonia loss; therefore reducing volatility requires a multi-faceted approach. Animal species, diet, housing, manure storing, grazing, and land application all influence ammonia volatility and are areas where specific mitigation techniques can be applied. An Environmental Protection Agency (EPA) national study (2005) showed that land application was the source of most ammonia emissions from dairy cow operations in the United States (Figure 1), making it the priority for research in better management practices.

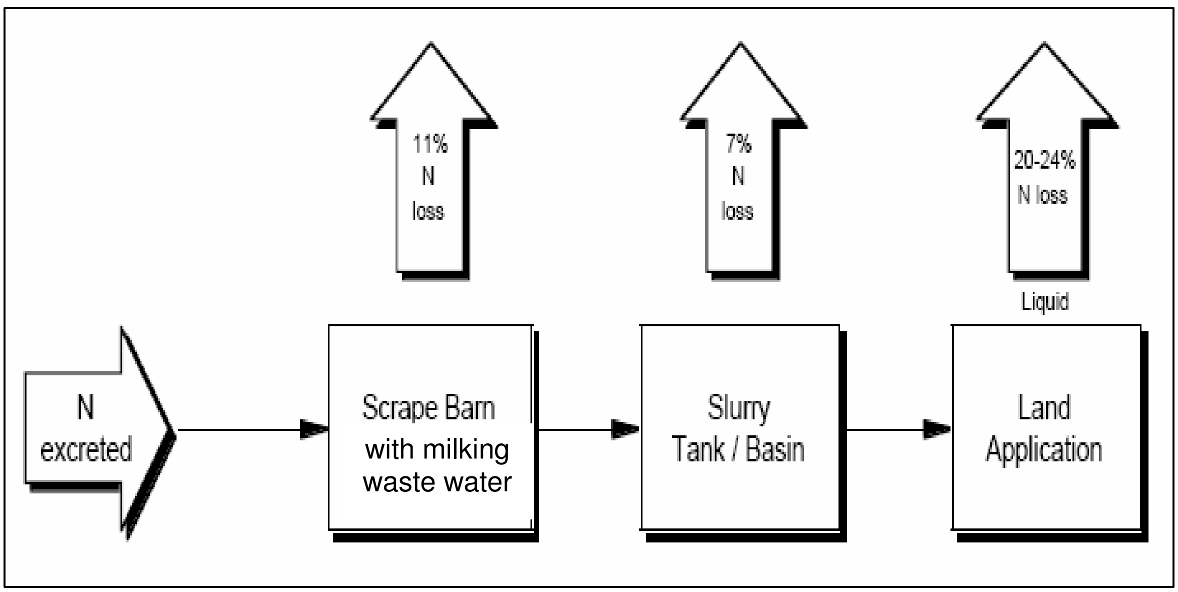


Figure 1. NH_3 emissions from dairy farms (EPA National Emissions Estimates, 2005)

The ultimate goal of ammonia mitigation is to convert ammonia to non-volatile nitrogen such as nitrite (NO_2^-), nitrate (NO_3^-), or to gaseous nitrogen (N_2). Proper management also means that the fertility needs of crops are met, but not exceeded.

Feed management, including reducing dietary crude protein, is one effective method of limiting the amount of nitrogen excreted from a dairy cow according to a study conducted at the US Dairy Forage Research Center in Wisconsin (Powell et al., 2007). Dairy cows typically have low nitrogen to milk protein ratios, meaning that only about 14–40% of consumed nitrogen is converted to protein and the rest is excreted in feces and urine (Hristov et al., 2004). Bussink and Oenema (1998) stated that “nitrogen retention” is only about 20% of “nitrogen intake,” while a 43% retention rate is theoretically possible.

Biofilters have been used and researched as a way to reduce ammonia volatility from animal housing (Keskiner and Ergas, 2001). The filters can be installed in the housing ventilation system to help keep animals (and farmers) from suffering lung damage due to ammonia-based $PM_{2.5}$ and to reduce emissions into the atmosphere. Another method for mitigation of ammonia from animal housing is to keep animal urine and feces separate which will, in turn, keep the majority of urea away from a high source of volatile N in feces. This method reduces total volatility, but requires additional expensive infrastructure. Another method for reducing volatility in animal housing is to frequently flush waste into a storage facility. The reduction of ambient exposure and addition of moisture to fresh manure reduces the volatility rate, but this method requires high water use. The previous two methods mentioned may also require a high level of maintenance (Ndegwa et al., 2008).

Another method for reducing ammonia volatility is to chemically treat the manure in storage with acidifying compounds to lower pH which limits urease enzyme activity; however, use of these manure additives have had mixed results. Acidification of slurry is only effective if the pH can be lowered to less than 5 (Bussink et al., 1994). Acidifying compounds include sulfuric acid (H_2SO_4), hydrochloric acid (HCl), and phosphoric acid

(Ndegwa et al., 2008). Phosphoric acid increases the P concentration in manure, making this an unattractive solution for manures in northeastern US where phosphorous pollutants are of particular environmental concern. One possible reason that urease inhibitors have not become popular for use by farmers is that their chemical effects on crops and pastures are unknown (Ndegwa et al., 2008).

Adding organic matter to manure immobilizes NH_4^+ and increases manure fertility for use by crops (Adams et al., 2004). Depending on the type of bedding material used in animal housing, the effect of N immobilization can be varied. A study by Powell et al. (2008) concluded that ammonia emissions from pine shaving bedding material was 20–25% lower than other bedding material tested (wheat straw, chopped newspaper, composted manure solids), perhaps due to the acidifying effect of the pine. The addition of organic matter to farmyard manure resulting in composted manure has an affect on the reduction of ammonia volatility when spread on land. Composted solids contain insignificant levels of NH_4^+-N that is the main source of NH_3 emissions. However, without an adequate carbon to nitrogen ratio of 30:1, ammonia volatility is actually increased in the process of composting (Amon et al., 2006).

Impermeable covers for stored manure provide a zero emissions rate during storage, but this merely increases the chances of volatility at the time of spreading (Ndegwa et al., 2008). Anaerobic microorganisms will readily produce ammonium under reduced conditions increasing the total ammoniacal nitrogen (TAN) content of manure. Liquid manure storage facilities typically emit less ammonia than dry manure stored in combination with different types of bedding (straw, sawdust, woodchips, etc.).

Of the many methods for reducing ammonia volatility, proper management of land application can be the most cost effective and have the greatest impact as well as "improving nitrogen utilization by crops" (Jokela and Meisinger, 2008). Depending on the farming operation, traditional incorporation of manure using a moldboard plow can have a great impact on reducing volatility as can direct injection techniques for perennial grazing systems. Broadcasting or even splash plate applications of manure are not considered ammonia reduction techniques because they increase air contact with manure while it is being applied to fields. Mechanical land application of slurry for ammonia emission reduction can be performed in many ways: trailing hose, trailing shoe, open slot injection, closed slot injection, s-tine cultivator, concave disc, or rapid incorporation of slurry by plough (Meisinger and Jokela, 2000; Webb et al., 2009). It is important to note that the efficacy of these methods is highly varied and therefore not entirely dependable without following application recommendations based on weather conditions. Ammonia volatility during land application is highly susceptible to ambient conditions. A review of ammonia reduction methods by Bussink and Oenema (1998) on the efficacy ranges of several land application techniques is summarized in Table 1.

Table 1. Efficacy of land application techniques for reduction of ammonia emissions from manure

Manure application technique	Range of efficacy %
Tine injection	95-100
Disc injection	80-100
Soil incorporation after surface spreading	35-95
Acidification prior to surface spreading	30-100
Band spreading	35-95
Dilution with a 1:3 slurry:water ratio	20-80

Special tillage implements for reducing volatility can be expensive and so a less attractive option to farmers. Another concern with land application is that increased nitrogen retention in soils (due to reduced volatility) can potentially have a polluting effect due to leaching. Manure application must be uniform and timely for the stimulation of crop growth to be most effective.

Table 2 provides an overview of practical considerations in the selection of ammonia abatement techniques for land spreading manures. These techniques are implemented by farmers in Europe as part of their commitment to emissions reduction. However, without a better understanding of environmental effects on ammonia volatility, the range in effectiveness of these methods will continue to be large.

Table 2. Methods of manure application on land. UNCLRTAP, *Good Agricultural Practice for Reducing Ammonia* (2001).

Abatement technique	**Manure type**	**Land use**	**Reduction in emission**	**Restriction on applicability**
Trailing hoses	Slurry and liquid manure	Grassland/ arable land	10–50%	Field slope, size and shape. Not viscous slurry. Width of tramlines for growing cereal crops. Height of crop is a factor on arable land
Trailing shoe	Slurry and liquid manure	Mainly grassland	40–70%	As above.
Shallow injection	Slurry and liquid manure	Mainly grassland	open slot 50-70% closed slot 70-90%	As above. Not stony or very compacted soils
Deep injection (including arable injectors)	Slurry and liquid manure	Arable land	70–90%	As above. Needs high powered tractor
Incorporation into soil	All manure types	Arable land including grass leys	20-90%	Land that is cultivated, preferably ploughed

Direct injection of manure, while dramatically reducing volatility of ammonia, requires an *increase* in energy use by farm machinery resulting in increased greenhouse gas emissions (Hansen et al., 2003). Injection application of manure may not be appropriate for use in Massachusetts as many dairy farm soils are very rocky (Table 2). More research of field scale applications of manure rather than simulations carried out in plots is necessary to get a better understanding of how these mitigation techniques will actually work for farmers (Webb et al., 2009).

Environmental Conditions Affecting Ammonia Volatility

Determining the best time for manure application to the field depends on crop type as well as environmental conditions favorable to reducing the chances of volatility. Bussink and Oenema, (1998) suggest that the optimum time for manure application in temperate climates that will have the least amount of ammonia loss is in the early spring when temperatures are low, rainfall is high, and crop growth has begun. This recommendation does not take into account the higher rates of nitrate leaching leading to eutrophication also common in the spring (particularly in the northeastern United States). Ammonia volatility is affected by several environmental conditions such as soil pH, soil cation exchange capacity (CEC), soil moisture content, wind speed, rainfall, and temperature. Sommer and Hutchings (2001) explained the relationship between the volatility of ammonia from manure to the atmosphere as follows:

> The concentration of NH_3 at the liquid surface is primarily a function of the chemical and physical conditions within the manure whilst the transfer of NH_3 from the air at the surface to the atmosphere is primarily a function of the local meteorological conditions.

"Chemical and physical conditions" within the manure and soil refer to pH, soil cation exchange capacity (CEC), moisture content, and urease activity. Transfer of ammonia from the manure surface to the atmosphere has to do with "meteorological conditions" such as wind speed, rainfall, solar radiation, and temperature. Because many environmental conditions have a direct or indirect effect on ammonia volatility, appropriate low cost management solutions can be developed by better understanding the effects of environmental conditions on volatility.

pH

Transformation of nitrogen in field applied manure is affected by the pH of the manure and the soil where the nitrogen converts to ammonium (NH_4^+) in acidic or neutral conditions and to ammonia (NH_3) in alkaline conditions (Gay and Knowlton, 2005). Ammonia volatilization from cow manure applied to soil increased linearly with soil pH in the range of 5.4 to 6.9 in an experiment conducted by Kemppainen (1989). Soils in the northeastern United States are typically acidic therefore pH effect on volatility is not of great concern to reduction of N losses (Meisinger and Jokela, 2000). Increases in manure pH from 7.7 to 8 will double the rate of emission (Sommer and Hutchings, 2001). United States manure tests for farmers do not typically report pH because its initial pH is insignificant and normally increases rapidly with soil contact (Meisinger and Jokela, 2000). Reducing ammonia volatility based on factors of pH is difficult due to the rapidly changing nature of manure and soil pH over time.

Wind Speed

Studies of surface-applied manure have shown that high wind speeds increase rates of volatility (Balsari et al., 2006; Sommer and Hutchings, 2001). In a study by Sommer et al. (1991), ammonia losses from fields with surface-applied manure increased significantly with a wind speed increase to 2.5 m s^{-1}. Another study showed that an increase in wind speed from 0.5 to 3.0 m s^{-1} over a five-day period increased ammonia emissions by 29% (Thompson et al., 1990). High wind speeds increase the mass transfer of air between the manure surface and the atmosphere, in turn increasing ammonia volatility. The greatest impact of wind speed on volatility is before manure dries and concentrations of NH_4-N have reduced (Meisinger and Jokela, 2000). Immediate incorporation of manure into the ground reduces the affect of wind speed on ammonia volatility as does waiting for a calm day for manure application.

Rainfall

Rainfall reduces ammonia volatility from field applied manure by encouraging infiltration of manure into the ground, but only if the rain occurs during or shortly after application and the ground is not frozen. Too much rainfall or spring snow melt will saturate a soil, making it impermeable to manure on the surface and encouraging runoff. A 30% reduction in ammonia emissions was reported by Pain and Misselbrook (1997) after 1.8 cm of rainfall on land spread with cattle slurry. A study by Sommer et al. (1997) concluded that trail hose application of manure tended to be less efficient on wet soil. Some emission reduction recommendations tell farmers to apply manure immediately before rainfall is expected, or to irrigate the field with water after application (Meisinger and Jokela, 2000).

Temperature

The effects of cold temperatures on volatility have not been thoroughly investigated however several papers indicate that there is a correlation between ammonia emission rates and temperature (Li et al., 2005, Yang et al., 2003; Sommer et al., 1991). Denmead et al (1982) stated that physical chemistry laws allow us to predict that ammonia losses will decrease by a factor of about 3 for each 10°C drop in temperature. Solar radiation that accompanies warming daytime temperatures increase NH_3 emissions in several ways: by increasing turbulence in the atmosphere which, in turn, increases transportation of NH_3 away from the soil surface; by increasing the evaporation rate of water from manure which increases the total ammoniacal nitrogen (TAN); and by increasing the temperature of the manure itself which increases microbial activity (Sommer and Hutchings, 2001). The effects of cold temperatures on ammonia volatility are less certain:

> Low but sustained emission rates resulting in high cumulative NH_3 losses have been observed at temperatures near freezing point (Thompson et al., 1987 and Sommer et al., 1991), but this probably reflects the slow infiltration of slurry into frozen soil (Sommer and Hutchings, 2001).

If cold temperatures significantly reduce ammonia volatility from surface-applied dairy manure, then some dairy farmers can apply manure later in the fall than they currently do at no extra cost while maintaining on-farm nutrient sources and reducing air pollution.

It is known that urease activity is low between 5 and 10°C and increases exponentially above 10°C (Braam et al., 1997). Ammonia found in dairy manure is produced as a result of urease enzymatic activity, and urease is produced by microorganisms abundantly present in feces (Powell et al., 2008). Several factors increase urease activity in manure including pH above 7, increased oxygen contact, lower water content, and increases in temperature (Powell et al., 2008). In one recent experiment, ammonia volatility increased incrementally at 4, 20, and 35°C, suggesting that microbiological processes play an important role in NH_3 volatilization (Van der Stelt et al., 2007), and that temperature effects on microbial activity are also significant. According to the Van der Stelt experiment, optimal growth temperature of bacteria producing the urease enzyme is about 37°C, which will increase volatility of ammonia. Cooler fall temperatures are expected to slow urease activity and, therefore, slow ammonia volatility. Postponing manure applications until air temperatures drop in late fall, but before the ground freezes may be effective in conserving more ammonia nitrogen for cover crop and crop use the following Spring.

Some research suggests that although cold seasonal temperatures reduce ammonia volatility by minimizing urease activity, warming spring temperatures will cause urea hydrolysis to increase and ammonia to be emitted again (Mulvaney et al., 2008). The process of freezing manure in the field is thought to have the same affect as drying, namely that it increases volatility (Lauer et al., 1976). Due to the large degree of uncertainty, more research on the effects of cold temperatures on ammonia volatility from manures is necessary.

In conclusion, no single environmental factor is the main driving source for ammonia volatility. Implementation of mitigation techniques for land application of manure requires an understanding of how chemical and meteorological processes interact to increase or reduce volatility. Models of ammonia volatility under field conditions can help to predict volatility behaviors of manures. Ammonia sampling techniques for modeling of emissions must be accompanied by meteorological measurements to reflect the various environmental effects.

Measuring Ammonia Volatility

Many sampling techniques have been developed in ammonia volatility research, but no single method has emerged as the industry standard in ammonia sampling, making the many experimental results difficult to compare. Two main categories have emerged in NH_3 sampling techniques: micrometeorological methods (usually used for large areas) and enclosure methods (frequently used on small plots for comparative experiments) (Misselbrook et al., 2004). Static chambers, dynamic chambers, and wind tunnels are all enclosure methods. Tunable Diode Laser (TDL), passive diffusion samplers (PDS), passive flux samplers (PFS), and absorption flasks are used in the micrometeorological method as well as the enclosure method.

With the chamber methods, a surface that emits ammonia is covered, and an acid trap is used to capture volatilizing ammonia. Without the use of an acid trap, air can be removed from the chamber with a syringe and analyzed by gas chromatography for ammonia content. In a dynamic chamber, air is blown through the system with a fan, whereas in a static chamber there is no fan, and in a wind tunnel the chamber allows air to flow freely or with a fan through the system with sampling units placed at the entrance and exit. Several variations to the enclosed system have been developed for different experiments, including the chamber used in this research. Tie-stall air emission chambers were developed to measure emissions from animal housing (Powell et al. 2008). In another study, Powell (2008) designed a dynamic chamber using PDS samplers to measure ammonia volatility in field simulations of manure application.

According to Hutchinson and Livingston (1993), emission rates of ammonia can be calculated for the enclosed chamber system by the following equation:

$$Q = V/A\ (C-C_0)/t$$

Where Q is the emission rate, V is the volume of the chamber, A is the area of soil covered by the chamber, C is the concentration of the gas in the chamber at time t, and C_0 is the initial concentration at time zero. This equation assumes that the gas concentration increases linearly with time inside the chamber. However, with changing concentrations and ambient conditions, the emission rate will also change in a nonlinear fashion over time (Li et al., 2000).

Enclosed chamber methods have been considered inaccurate for measuring ammonia volatility under field conditions because the chamber alters environmental conditions inside the chamber if sampling over long periods of time (Mulvaney et al., 2008). Static chambers in particular tend to cause negative feedback, or conversion of NH_3 back to NH_4^+ within the system, particularly right after spreading manure when emission rates are high (Misselbrook et al., 2005). A solution to this undesired effect is to shorten sampling periods to one or two hours instead of 24 hours (Powell, 2008), and to move the chambers to a new location for every sampling period (Misselbrook et al., 2005). Overall, enclosed chambers reportedly estimate higher emission ranges than meteorological methods (ECETOC, 1994), most likely because chambers collect emissions closer to the source than the micrometeorological method.

PDS, PFS, or absorption flasks are fairly small and portable samplers used in the micrometeorological method. The PDS and PFS use acid-coated Teflon beads or acid-coated paper to trap ammonia as air passes through. Absorption flasks are glass tubes coated on the inside with acid to capture ammonia as air passes through the tube. These samplers are typically attached to masts strategically located within large experimental plots (at least 20 by 20m) at varying heights from the ground. A mast upwind from the plot measures ambient ammonia concentrations. All masts should be equipped with a weather station or data logger to measure ambient wind speed, air temperature, and rainfall. A problem identified with the efficacy of these micrometeorological methods is that they depend upon atmospheric dispersion models or mass balance integrated horizontal flux techniques that depend weather conditions that may change unpredictably (Ergas et al., 2000).

For most ammonia samplers, whether in combination with the enclosure method or the micrometeorological method, an acid trap is used to capture volatilizing ammonia. In a study by Rabaud et al. (2001), oxalic acid, tartaric acid, sulfuric acid, or citric acid were all found to be equally capable at capturing ammonia, and no single acid was preferred over others.

Conclusion

Ammonia emissions worldwide have been deemed a global pollutant affecting not only air quality, but also water eutrophication, terrestrial ecosystem enrichment, and global warming (Aneja et al., 2008). Global agreement in reinforcement of reduction techniques is varied, with the EU leading the way in ammonia emissions mitigation. Other than reducing the total number of animals on farms, proper land application of manure has the greatest impact on ammonia emission reduction. Direct injection of manure slurry into the soil has the greatest ammonia emission reduction capability, although direct injection is not ideal or cost effective for all locations. For example, Massachusetts soils tend to have a high quantity of rocky glacial till unsuitable for direct injection. Ammonia reductions from land application of manure are greatest when applied under ideal environmental conditions. Ideal chemical and meteorological conditions for ammonia reduction under any application technique are: low manure and soil pH, high CEC soils, little or no wind, some rainfall, and cool but not freezing temperatures (Bussink and Oenema, 1998; Meisinger and Jokela, 2000; Sommer and Hutching, 2001). The presence of a growing crop is also ideal for nitrogen uptake to reduce ammonia volatility. These “ideal” conditions never exist simultaneously for all practical purposes of manure application, but can serve as guidelines for choosing less volatile conditions over more volatile ones. Sampling methods that quantify ammonia emissions around the world fall into two major categories– enclosure and micrometeorological (Misselbrook et al., 2004).

Based on the literature read for this review, more work is required in the following areas of ammonia volatility research:

1) Better and more comprehensive data on critical levels of emissions present in the atmosphere in locations around the world is needed to provide a better global estimate of ammonia emissions. Global atmospheric pollutants require international oversight to reach better agreement on emissions reduction goals worldwide (Galloway et al., 2004).

2) There is a need to reinforce effective low-cost ammonia mitigation techniques for farmers and identify new ones (Hansen et al., 2003; Amon et al., 2006; Aneja et al., 2008).

3) More research in field-scale manure application for reduction of N losses is required for practical consideration by farmers (Webb et al., 2009).

4) More seasonal and long-term data collection and research is required to better understand changes in ammonia emission rates throughout the year in different regions around the world (Powell et al., 2008).

5) More accurate modeling and experiments designed to address the interactive affects of environmental conditions such as pH, CEC, wind speed, temperature, and rainfall on volatility are necessary (Jokela and Meisinger, 2008).

6) Accurate, simple, and low-cost sampling methods are required to ensure continued research and oversight of ammonia emissions (Misselbrook et al., 2004).

Research conducted for this thesis provided more information on several of the six focus areas mentioned above. A low-cost method for reducing ammonia volatility and retaining nutrients in dairy slurry was explored. Dairy farmers in Massachusetts could reduce ammonia volatility by spreading manure on cover-cropped land during the fall if environmental conditions for reduced emissions include low manure and soil pH, high CEC soils, little or no wind, some rainfall, and frozen temperatures. This review and associated experiment on fall volatility rates from field applied manure in Massachusetts makes an important contribution to ammonia emissions research that to date lacks seasonal data. Finally, a simple and low-cost dynamic chamber for sampling ammonia volatility was designed for this research and can be used for future studies in ammonia volatility.

CHAPTER II

ASSESSMENT OF AMMONIA VOLATILITY FROM FALL SURFACE-APPLIED LIQUID DAIRY MANURE

Introduction

As ammonia concentrations in the atmosphere continue to grow and cause significant amounts of pollution (Galloway et al., 2000), the United States has followed Europe in monitoring and limiting ammonia emissions from animal operations including dairy farms (Henry and Stowell, 2009). To meet new emission standards as well as to reduce pollution, it is evident that practical and low cost ammonia mitigation strategies must be identified for use by farmers. Manure is a valuable source of micro- and macronutrients for crops, and if managed properly can provide most of a farm's fertility needs. Manure can provide all the phosphorous and potassium needs for crops, but is frequently an inadequate supply of nitrogen (Herbert, 2002). Increasing nitrogen efficiency by reducing ammonia volatility is important in gaining the most benefit from manure since about one half of the nitrogen content in liquid dairy cow manure is in the form of volatile ammonium (Jokela and Meisinger, 2008) (Figure 2).

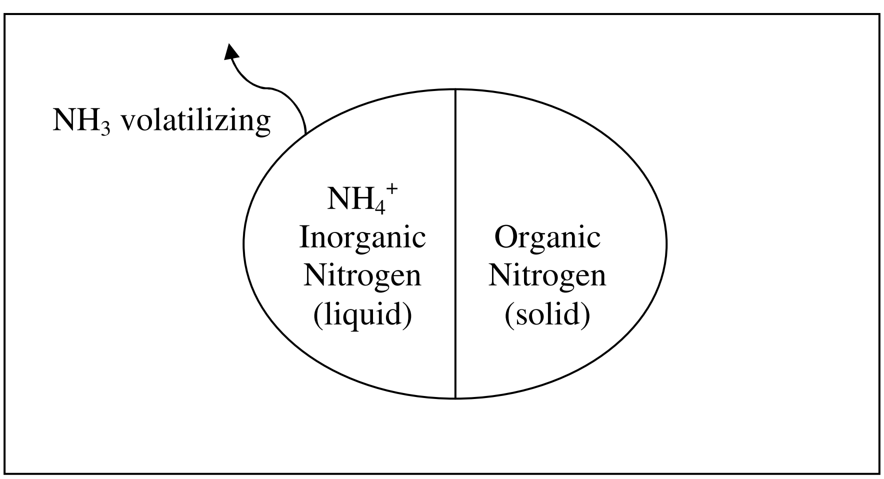


Figure 2. Ammonia nitrogen loss from surface-applied dairy manure

The ammoniacal portion of manure is subject to volatilization, nitrification, binding with cation exchange sites, accumulating in plant tissue, or becoming immobilized by soil microbes. The organic portion of nitrogen is tied up in undigested plant matter and takes from a period of months to years to decompose and undergo ammonification (Sylviaet al. 2005). Retaining more ammonia for use by plants improves the nitrogen to phosphorous ratio by increasing the nitrogen content of the manure, helping to reduce the potential for phosphorous contamination of waterways common in Massachusetts. Nitrogen retention from manures also helps the farmer financially by providing all the crop's needs without the use of expensive chemical fertilizers.

As mentioned in the previous chapter, little research has been conducted on using environmental indicators for timing applications of dairy manure to reduce ammonia volatility; a mitigation solution which would be of no extra cost to the farmer. Data regarding ammonia volatility in the fall from fields planted with cover crop and spread with manure is also lacking, particularly in Massachusetts where most dairy farms are small in size and in terms of an operating budget. As identified in the previous chapter, there is a need to reinforce effective low-cost ammonia mitigation techniques for farmers and identify new ones (Hansen et al., 2003; Amon et al., 2006; Aneja et al., 2008). Low cost ammonia mitigation techniques require minimal energy and infrastructure inputs for the farmer; such as applying manure to fields under appropriate weather conditions and to a growing crop. In Massachusetts, more seasonal, long-term data collection and research is also required to better understand changes in ammonia emission rates throughout the year.

Although rapid incorporation of manure is proven to greatly reduce ammonia volatility, many farmers in Massachusetts simply do not have the time to harvest a crop, plant a cover crop, and spread manure all at once at the end of the season. Due to lack of manure storing capacity, farmers are required to empty their storage tanks twice a year; typically in the fall and spring. In Massachusetts, manure application to harvested fields in rainy weather in the fall or early winter without incorporation has traditionally been discouraged due to the high potential for N and P losses to surface water from runoff on frozen ground (Herbert, 2002). However, if manure is applied and incorporated to fields without a cover crop, the nitrogen applied will likely be lost to nitrate leaching. Therefore, manure application must be timed to coincide with early cover crop planting (late August to early September) in the fall to maximize N accumulation as the crop grows and before leaching or runoff occurs. Applying manure to fields with a growing crop is one aspect of best manure management practices. One study concluded that slurry applied to a growing crop or to grassland abates ammonia volatility more so than applying slurry to bare ground or crop stubble (Malgeryd, 1998; Smith and Misselbrook, 2000). A suggested management practice based on the results of this research would be to broadcast a seeding of cover crop while harvesting an annual crop in one pass over the field, and to return later in the fall to apply manure when the farmer had more time.

The primary goal of this research was to investigate a management strategy for mitigating ammonia volatility from cow manure at the time of field application with no incorporation in the fall before snow fall. The specific research question to be answered was: Do cooler fall temperatures have an effect on reducing ammonia volatility from surface-applied liquid dairy manure? The hypothesis is that application of manure in cooler fall temperatures will slow the rate of ammonia volatilization, making more nitrogen available to cover crops for uptake in the fall or early in the spring resulting in an overall higher retention rate of nitrogen for use by crops in the following growing season. The overall objective of this research was to identify low cost manure management options that dairy farmers can maintain as an on-farm nutrient source by reducing ammonia volatility from their manure. This objective was achieved by studying the effect of temperature on ammonia volatility from surface-applied liquid dairy manure applied every month over a period of four months from September to December, 2008. Manure was surface-applied to a field cover cropped with winter rye (*Secale cereale* L.) on the UMASS Extension recommended date of September 15th. Ammonia was measured using a dynamic chamber method. Results showed ammonia losses in December were about one fifth of the losses encountered in September.

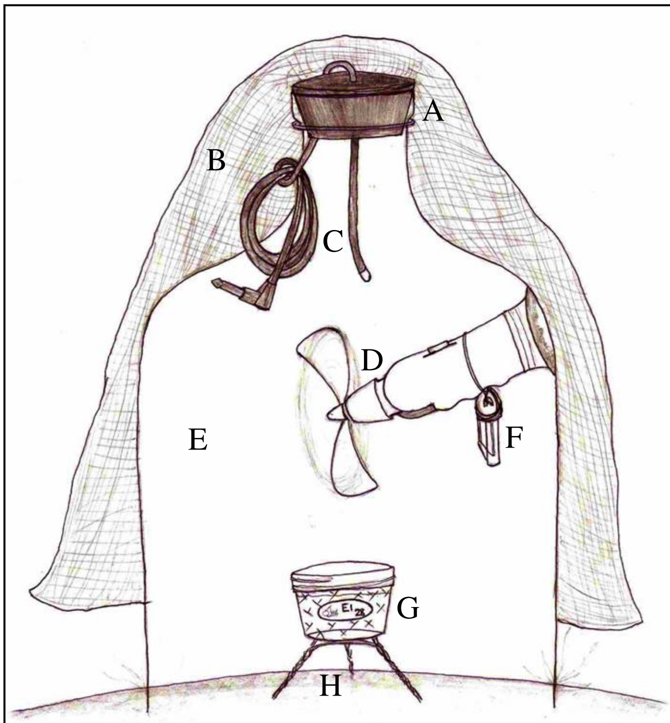
Secondary goals of this research involved studying changes in the nutrient content of liquid manure over a period of four months while it remained in storage, and following the nitrogen cycle after application to the soil by analyzing the N content in the soil's cover crop rhizosphere (approximately 0-30cm deep) and in the leafy portion of cover crop tissue to evaluate nitrogen retention for crop use in the spring. Manure samples from the storage tank increased in nitrogen content with each month of application. Ammoniacal nitrogen contributed to this increase as the N content in storage tank manure increased over the period of four months, while other nutrient concentrations fluctuated or remained the same. Soil samples were collected from under the surface-applied manure over the period of the experiment to determine changes in nitrate concentrations and in the spring to determine retained nitrogen. Cover crop tissue samples were taken over the period of the experiment also to measure levels of total nitrogen uptake from the soil and manure applied to them and again it the spring to determine nitrogen retention.

The nitrogen cycle is fairly complex (Appendix A), and it is challenging to fully understand nitrogen losses and gains from a field whose surface has been applied with liquid dairy manure over a period of four months (September-December, 2008) and then to calculate nitrogen retention from these manure applications after the winter in April, 2009 still available for use in the next growing season. Nonetheless, soil nitrate levels in the spring showed greater retention rates from the December application than the September application of manure. Tissue total nitrogen contributions to the field in April, were more varied than soil results and did not contribute a great deal to the nitrogen retention. The soil and tissue nitrogen content in April of 2009 represent retained nitrogen, while ammonia measured during the fall of 2008 contribute to the faction of nitrogen lost from the field applications. Overall results from the ammonia losses showed a reduction in ammonia volatility with reducing temperatures every month. More manure nitrogen is mineralized and nitrified; retained as nitrates in the soil than as total nitrogen in the cover crop tissue. Spring tissue nitrogen concentrations in all plots are lower than during the fall, suggesting that nitrogen is being stored in the plant roots and not completely transferred to the leafy portion by April 10, 2009. Uncertainties remain about whether the nitrogen is, in fact, reserved for use by crops, or if it is leached or lost to long term ammonia volatility that is below the detection limit of the method of measurement used in this research. A large majority of the nitrogen applied in the form of manure on all treatment plots is unaccounted for by the time spring samples were taken; meaning it was either lost from the cropping system, or converted to a form not sampled in this research such as leachate or root biomass-N.

Materials and Methods

Ammonia Volatility Chamber

Given the small scale of this experiment (plots smaller than 400m^2), the chamber method for sampling ammonia emissions was chosen. After preliminary experimentation with several methods, six dynamic chambers based on several designs (Cooper et al., 1990, Li et al., 2000, Misselbrook, 2004, and Powell, 2008) were constructed for use in this research (Figure 3). This dynamic chamber method proved to be inexpensive and reliable at measuring relative quantities of ammonia volatilizing in a variety of field conditions.



A. Size 12 rubber stopper
B. 50% shade cloth
C. Thermistor
D. D-cell battery-operated fan with mounting base
E. 20-liter carboy with the bottom cut off
F. Onset UA-002-64 light and temperature data logger
G. 4 oz. Ball jelly jar containing 50 ml of 0.02 N H_2SO_4
H. Steel wire tripod

Figure 3. Ammonia Volatility Chamber based on the dynamic chamber method

The chamber is constructed from a 20-liter carboy (E) with the bottom removed and pushed several centimeters into the soil surface to provide a seal near the ammonia emitting surface. Glass was chosen as the material for the chamber walls because other materials such as plastic and aluminum absorb ammonia. A 50% shade cloth (B) was used to cover the carboys to minimize a greenhouse effect. A thermistor (C) tightly fitted through a size 12 rubber stopper (A) covered the opening in the top of the carboy and was one of two methods used in recording the temperature inside the chamber. Inside the chamber a D-cell battery-operated fan with mounting base (D) was secured to the chamber wall with marine-based epoxy glue. Batteries were replaced in the fans at the beginning of each sampling period or once a month. An Onset UA-002-64 light intensity and temperature data logger (F) attached to the fan with dental floss is the second method for recording temperatures inside the chamber. The ammonia sampling container rests on a steel wire tripod (H) 10 cm above the ground surface so as to avoid contact with the manure or the fan blades. The sampling containers are 4 oz. Ball jelly jars (G) containing 50 ml. of 0.02N sulfuric acid (H_2SO_4).

Sampling containers were exposed to the ambient conditions inside the chamber with the fan operating for one hour at a time to reduce the effect of a feedback cycle in which ammonia concentrations became too high within the chamber and condensed or reverted back to ammonium (Misselbrook et al., 2005 and Powell, 2008). The chamber was moved to a different manured surface within the plot for every sampling period of one hour. Ammonia gas (NH_3) volatilizing from the manure and into the chamber is highly hydrophilic and diffuses from the chamber atmosphere into the sampling jar containing 0.02N sulfuric acid (H_2SO_4) converting the gas to ammonium (NH_4^+). This concentration of sulfuric acid was chosen because it can be directly analyzed in the lab without further preparation, and is fairly non-toxic or corrosive for use in the field.

Location and Plot Design

Research was conducted at the University of Massachusetts Crop and Animal Research and Education Center (CAREC) in South Deerfield, Massachusetts from September-December 2008. A 10.668m wide by 38.1m long (35ft by 125ft) experimental area with no recent history of manure application was used for this experiment. The soil type, Hadley fine sandy loam, is typical of the surrounding farmland with a bulk density of 1.3g/cm^3. Each treatment plot was 1.5m wide by 7.6m long (5ft by 25ft), distributed in a randomized complete block design with three replicated manure treatments each month and three control plots (Figure 4). Manure application and sampling periods were repeated at the beginning of each month for four months (September-December 2008). Manure was applied to three replicate plots each month on or near the first of the month and sampled over a period of five days following. The layout of the experiment is shown in Figure 4 below.

	guard	guard	guard	guard	guard	guard	guard
Rep.3	guard	Sept.	Cont.	Oct.	Nov.	Dec.	guard
Rep.2	guard	Dec.	Oct.	Nov.	Cont.	Sept.	guard
Rep.1	guard	Nov.	Sept.	Dec.	Oct.	Cont.	guard
	guard	guard A	guard B	guard C	guard D	guard E	guard

Figure 4. Randomized complete block experimental design

Winter rye (*Secale cereale* L.) was hand seeded as a cover crop on all plots on September 15th including control plots at a rate of 100kg/ha (90lbs/ac). This is the planting date recommended by UMass Extension for adequate nutrient uptake in fields cultivated for silage corn. Control plots did not receive a manure application but the soil and tissue was sampled regularly with all other plots. Guard plots were not planted with the cover crop or treated with manure, but were weeded and acted as a marker to prevent external disturbances.

Manure Application

Liquid manure was obtained from a nearby dairy farm owning a slurry tank. 'Liquid dairy manure' refers to a mixture of dairy cow urine, feces, and water with a water content of greater than 90%. The water content comes from a flushed or scraped barn floor with a pipe system that flushes the barn floor effluent into a storage tank. Bedding material for this dairy farm is woodchips, which was noticeable when the manure was surface-applied in this experiment. Appendix B includes photos of the dairy operation with manure storage, animals, and flush barn where manure for this experiment was collected as well as the method for collecting manure from the storage tank. Manure was pumped into four 113.56 liter (30gallon) trash barrels from the bottom of the slurry tank and transported to the experiment location at CAREC in South Deerfield one day before application. Liquid dairy manure was applied on September 2nd, October 2nd, November 3rd, and December 2nd, 2008 and monitored for ammonia volatility for one week after each date of spreading. Immediately prior to each application, a manure sample was taken and frozen then sent to the University of Maine Analytical Lab to be analyzed according to their standard manure test for percentages of moisture, total nitrogen, ammonia nitrogen, organic nitrogen, total phosphate, potash, copper, and zinc.

Several methods of manure application were tested and method B (Figure 5) was chosen for this experiment due to its uniformity and repeatability.

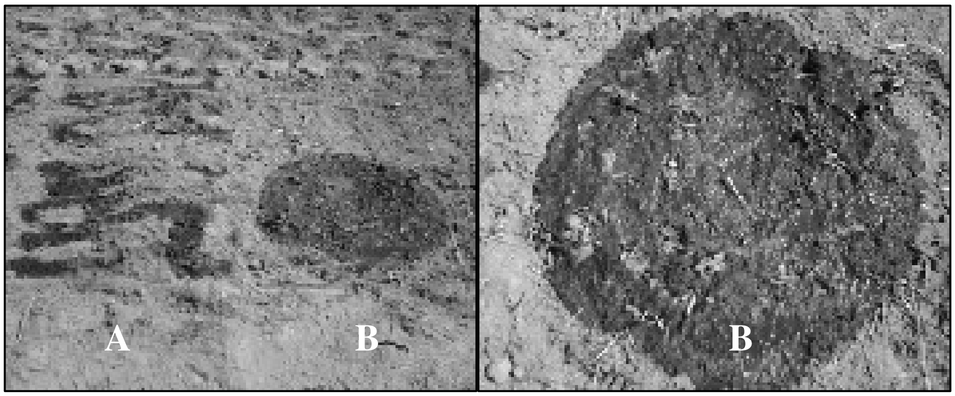


Figure 5. Different experimental manure application techniques

Method A (Figure 5) did not allow for the same amount of manure to be covered by the chamber for each sampling time while method B (Figure 5) resulted in approximately 1 liter of manure under the chambers at every sampling time. The circular manure applications averaged an area of 0.2 m^2 each with approximately 3.26 liters manure in each 'plop' resulting in measurements taken from an application rate of 16.19 liters of manure/m^2.

To ensure uniform application, a 1.5 m by 1.5 m (5 ft by 5 ft) square made of 1.75 cm (0.5 in) PVC pipe was divided with string into 4 m^2 (6.25 ft^2) sections and used as a grid. The PVC pipe grid was flipped five times down the length of the plot to create 20 manure sampling sites per plot. Using gallon (3.8 liter) milk jugs with the tops removed, 3.26 liter (0.861 gal) of manure was poured in the center of each section to achieve a uniform distribution for every sampling unit (Figure 6).

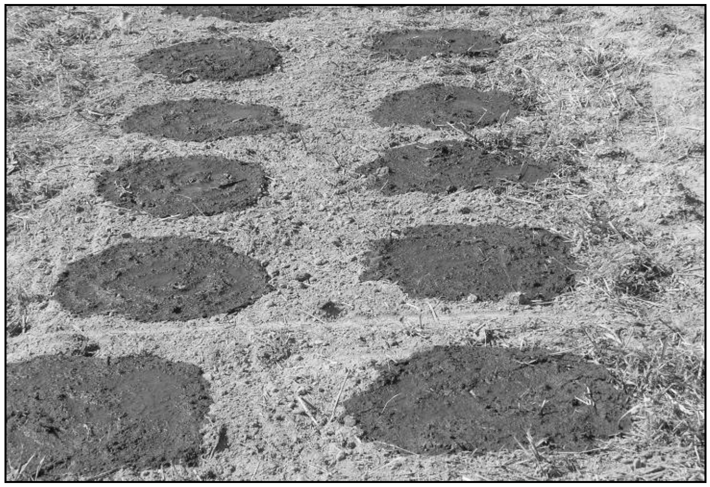


Figure 6. Uniform application of manure at a rate of 16.19 liter/m^2 in September, 2008

The ammonia volatility chambers covered a 0.06 m^2 surface area or 1 liter of manure in the center of each manure application, and were moved to a new location at the beginning of each hour of sampling so that the manure being sampled was exposed to ambient conditions and not influenced by chamber conditions. Appendix C provides a photographic description of how manure was applied to the field and consequently sampled for ammonia volatility in this experiment.

Manure was concentrated in circular applications at the recommended rate of 56,000 liter/ha (6,000 gal/acre) (Beegle, 1997), however was sampled at a rate of approximately 159,800 liter/ha (17,000 gal/ac) because the chamber covered this higher concentration of manure. Experimental results and discussion are based on the 159,800 liter/ha application because that is the rate from which sampling occurred. Recommendations for field application to farmers will be based on a 6,000 gal/ac application rate. According to Jokela and Meisinger (2004), the nitrogen content of 30 random liquid dairy manure samples analyzed by the Agricultural and Environmental Testing Lab at the University of Vermont averaged 25 lbs N/1,000 gal. Therefore to meet the crop nitrogen needs of 150 lbs N/ac, manure was applied at a rate of 6,000 gal/ac to simulate a farmer's rate of application.

Measurements

Ammonia Volatilization

Immediately after surface application in each replicate plot, a chamber was placed over the manure treatment with a sampling jar of 0.02 N H_2SO_4 for one hour. The first eight hours of the monthly sampling schedule were identical to the example for the month of September as shown in Table 3 below. After the first day, or eight hours, sampling at equal time intervals became impractical.

Table 3. Ammonia emission measurement schedule for one plot in September

Sampling Date	Sampling Time	Sample ID
09/02/08	09:00 - 10:00	1
	10:00 – 11:00	2
	11:00 – 12:00	3
	12:00 – 13:00	4
	13:00 – 14:00	5
	14:00 – 15:00	6
	16:00 – 17:00	7
	17:00 – 18:00	8
09/03/08	08:00 - 09:00	9
	14:00 – 15:00	10
09/04/08	11:20 – 12:20	11
09/05/08	12:40 - 13:40	12
09/08/08	10:40 – 11:40	13

Steps taken at the beginning of each measurement period were:

- record the date and time
- turn on the fan
- place the tripod in the center of the sampling area
- remove the lid from a new sampling jar and place it on the tripod
- carefully place the chamber over the sampling jar, and twist it into the manure surface approximately 2 cm

After one hour, to complete the measurement:

- record the time again
- record the thermistor temperature
- remove the chamber and replace the lid on the sampling jar, being careful not to drop any residue into the jar or spill any acid
- turn off the fan

These steps were repeated for all 96 samples over a period of five to eight days each month. At the end of the sampling period each month, all ammonia chambers and sampling jars were thoroughly cleaned with soap and water for use in the next month's experiment. The last sample was taken 146.33 hours after spreading manure in September, 122.33 hours after spreading in October, 121.5 hours after spreading in November, and 147.33 hours after spreading in December. This variability in sampling times had to do with when researchers were available to take samples. Appendix D shows a sample field data sheet from the month of October.

Soil

Soil and cover crop tissue was also sampled periodically. Soil samples were taken from each plot on the day before or immediately before spreading manure (called day '0'), 10 days after spreading, and 20 days after spreading and again in the spring after snow melt. Only the sample from 10 days after spreading could be taken in December because the ground was frozen during the other sampling times. The spring sample was taken April 10th, 2009 to represent the soil condition at the beginning of a farmer's growing season. Samples were taken after carefully removing the surface layer of manure and cover crop so as to sample only the soil. A composite of five core samples was taken at 0-15 cm and mixed together to get one representative sample for each treatment plot every month from September-December, 2008. Another composite sample at 15-30 cm was taken from each plot by inserting the soil core sampler into the hole made by the 0-15 cm sample. In the spring, a composite sample was taken from all treatment plots including the control plot that was planted with cover crop but received no manure application.

Cover Crop Tissue

Cover crop tissue was sampled from each plot at the same time every month starting October 30th after the cover crop had become well established and ending December 30th was analyzed for Total Kjeldahl Nitrogen (TKN). A spring sample was also collected on April 10th, 2009 to determine TKN transported to the leafy portion of the plant after winter. Two 0.09 m^2 (1 ft^2) samples from each plot were taken at ground level carefully leaving any soil behind, to make a representative sample of 0.186 m^2. Fresh weights and dry weights were recorded before grinding the tissue for analysis of TKN content.

Sample Analysis

Ammonia samples were analyzed by Flow Injection Analysis (FIA) in a Lachat Instruments QC 8500 Spectrophotometer. This instrument has a low threshold of 0.1 mg N/L, which limits the number of days ammonia sampling can continue after spreading manure (Hofer, 2003). Ammonia dissolved in the 0.02 N H_2SO_4 from field sampling jars (Figure 3) was analyzed directly in the FIA Method 12-107-06-2-A. FIA was also used to analyze tissue samples for Total Kjeldahl Nitrogen (TKN). Soils were analyzed for nitrate content by FIA. All sample analysis was conducted with the same instrument using different procedures and manifolds.

To analyze soils for nitrate: eight grams of soil were dissolved in 40 ml of 2 mM Calcium Chloride ($CaCl_2$) and mixed at 180 rpm for 15 minutes. Soils were filtered through Whitman number 2 filter paper and analyzed for NO_3 content by FIA Method 10-107-04-1-D (Sechtig, 2003). To prepare cover crop tissue for analysis, a 200 mg sample which had been ground with a Tecator Cyclotec 1093 Sample Mill was digested in 3.5 ml H_2SO_4 with 1.5 g potassium sulfate and 0.125 g cupric sulfate then diluted in 40 ml deionized water for analysis by FIA Method 13-107-06-2-D (Diamond, 2001).

Statistical Analysis

Data were analyzed using the SAS statistical software (SAS institute, 2006) by ANOVA using treatment, block, and date as the main effects. Also, an correlation between temperature and total volatility as well as rates of volatility explained if there are any significant relationships between changes in chamber temperature and changes in volatility from month to month. Similarly, soil nitrate amounts and tissue TKN amounts were statistically analyzed to see if there were significant differences in spring nitrogen retention depending on the month of manure application.

Results and Discussion

Ammonia, manure, soil, and tissue samples were all analyzed and the results from each data set are graphically presented and discussed separately in this section. At the end, the data are summarized together for a complete picture of the nitrogen retained, lost and unaccounted for. Reduction of ammonia volatility is only practical to the dairy farmer if the reduction in ammonia losses means increased nitrogen availability to crops. From an environmental pollutant and eutrophication perspective, reductions in ammonia volatility are only effective if that nitrogen is cycled through the cropping and farm system, and not lost by other pathways such as nitrate leaching. Therefore, in addition to a discussion of the affects of temperature on ammonia volatility, a comparison of measured losses to retained nitrogen in soil and cover crop tissue is made to calculate the nitrogen efficiency of each month's manure application. Also, a large portion of total nitrogen applied each month was unaccounted for after the completion of the research due to the inability to measure and analyze all the potential nitrogen sinks. This unaccounted portion of the total nitrogen applied shall be referred to as "potential loss". The chamber method for measuring ammonia volatility was capable of measuring relative amounts of volatilizing ammonia from month to month but not total amounts, therefore results are to be compared within this experiment and not to data gathered from other methods or experiments.

Ammonia sampled in the fall of 2008 demonstrated a reducing trend in volatility from surface-applied liquid dairy manure with each month of sampling from September through December 2008 (Figure 7).

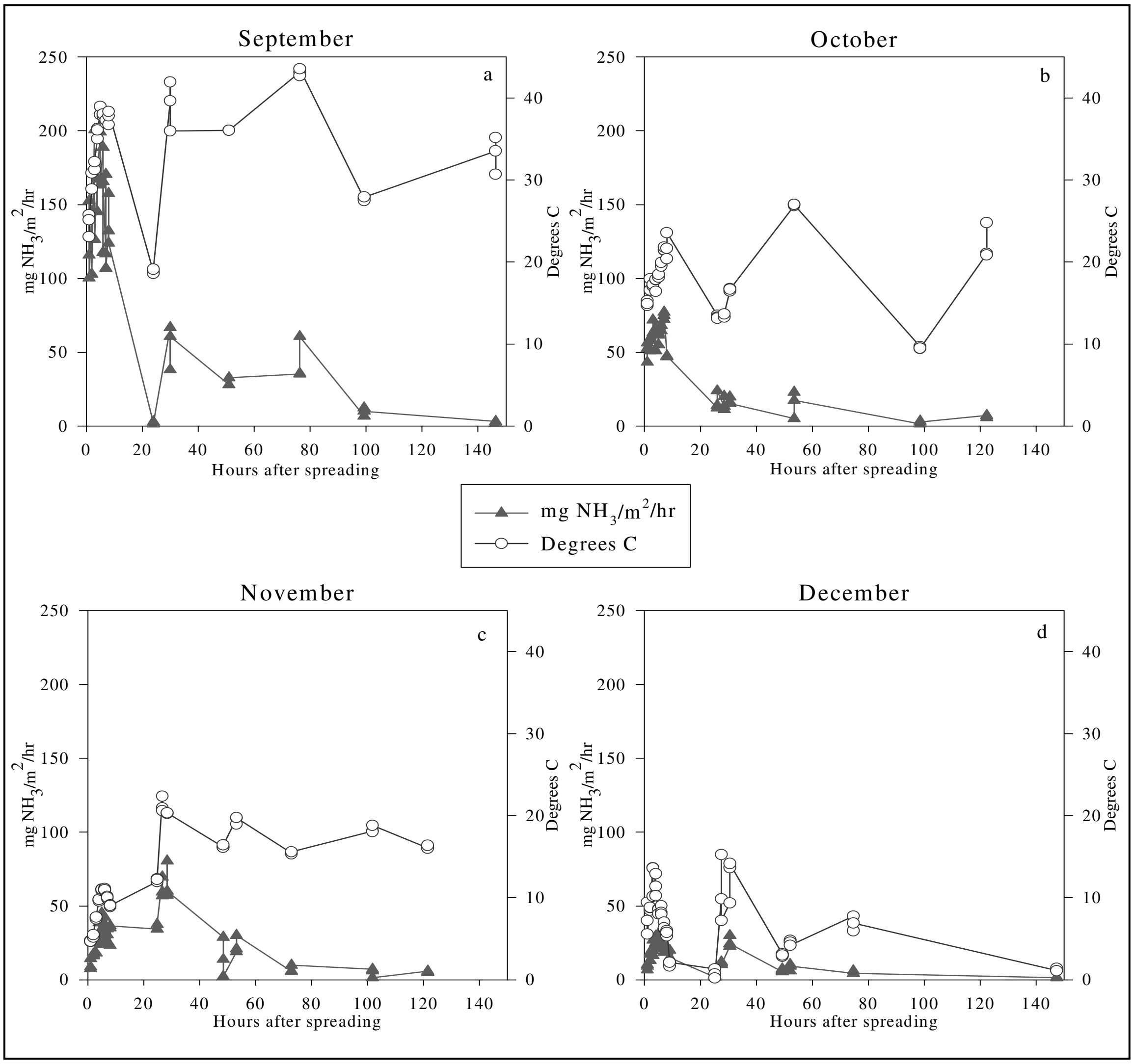


Figure 7. Rates of ammonia volatility and chamber temperatures for each treatment month: a. September, b. October, c. November, and d. December in 2008

The warmest temperatures and highest rates of volatility were recorded in September (Figure 7a). October (Figure 7b) and November (Figure 7c) had similar temperatures and rates of volatility, and December's (Figure 7d) application of manure produced the least amount of volatilized ammonia with the coldest recorded temperatures. Manure was applied to frozen ground in December, but there was no snow. Volatile ammonia losses did not follow a linear trend or form a decaying curve, but rather, was related to changes in temperature. Colder temperatures reduced the rate of ammonia volatility from surface-applied liquid dairy manure while warm temperatures increased the rate. In November (Figure 7c), the highest rate of volatility occurred on the second day after manure application, while the highest temperature recorded during this month's sampling period occurred on this day also.

The highest rates of ammonia volatility occurred in the first 24 hours after spreading in all months accept for November. These trends are concurrent with results from other experiments by Meisinger and Jokela, 2000 and 2008. Ammonia volatility could continue at very low rates past the 120-150 hour sampling period each month; however a more sensitive method of measurement and an analyzer capable of detection in the range of ppb is required to continue monitoring ammonia emissions (Li et al, 2000). Other factors influencing the accuracy of these results are three missing samples from the month of September where the sampling jar with acid was spilled in the field, left in the chamber for 2 hours instead of 1, or the chamber fan fell into the manure during sampling. The first sample taken in December is also inaccurate because the chamber was accidentally left to sample ammonia for half an hour instead of one hour. Due to missing data points, a 'ProcGLM' ANOVA (SAS 9.1) was conducted to analyze statistical significance of ammonia reduction in relation to temperature from month to month.

A spline curve analysis (SigmaPlot 8.1) of the area under the data points on the graphs in Figure 7 above for each month gave an approximation of total mg NH_3/m^2 lost from each month's application of manure. In September, a total 5131 mg NH_3/m^2 (46 lb/ac) was lost over 146 hours and the average temperature was 33.61°C. In October, a total 1838 mg NH_3/m^2 (16 lb/ac) was lost over 122 hours and the average temperature was 18°C. In November, a total 2614 mg NH_3/m^2 (23 lb/ac) was lost over 122 hours and the average temperature was 13°C. In December, a total 1028 mg NH_3/m^2 (9 lb/ac) was lost over 147 hours and the average temperature was 7°C. The correlation coefficient, r, relating average air temperature in the chamber over the entire sampling period to total ammonia volatilized each month is 0.91. This R value is significant at probability (P) < 0.0001.

Percent ammonia losses of the total ammoniacal nitrogen (TAN) applied from the manure each month can be calculated as follows:

$$\%L = 100 \times (NL/TAN)$$

where %L is percent ammonia loss, NL is total measured ammonia losses as calculated by spline curve analysis and reported as mgNH_4-N/m^2, and TAN is total ammoniacal nitrogen applied each month. Over the period of 146 hours sampled, September's measured losses totaled only 20% of the available ammonia applied. Other studies have reported up to 90% ammonia losses from surface-applied manure without incorporation (Stevens and Laughlin, 1997; Meisinger and Jokela, 2000; Huigsmans, 2003). The lower rate reported in this research could be due to chamber inefficiency, recently plowed soils that increased manure soil contact, or a low soil pH. In October a measured 7% of the TAN applied volatilized, while in November a measured 9% of the TAN applied volatilized. Several centimeters of rain were recorded on the first and second day of sampling in October while no rain was recorded during any other month's sampling period. Rain in October could have increased percolation of liquid manure below the soil surface reducing volatility potential. In December, 3% of total ammoniacal nitrogen applied was lost during the time of sampling.

An ANOVA analysis resulted in highly significant correlation between total ammonia losses and average temperatures over the four months of sampling (September-December). This overall result justified a closer look at the volatility rates and changes in temperature that occurred in the first eight hours each month when sampling times were equal (Figure 8).

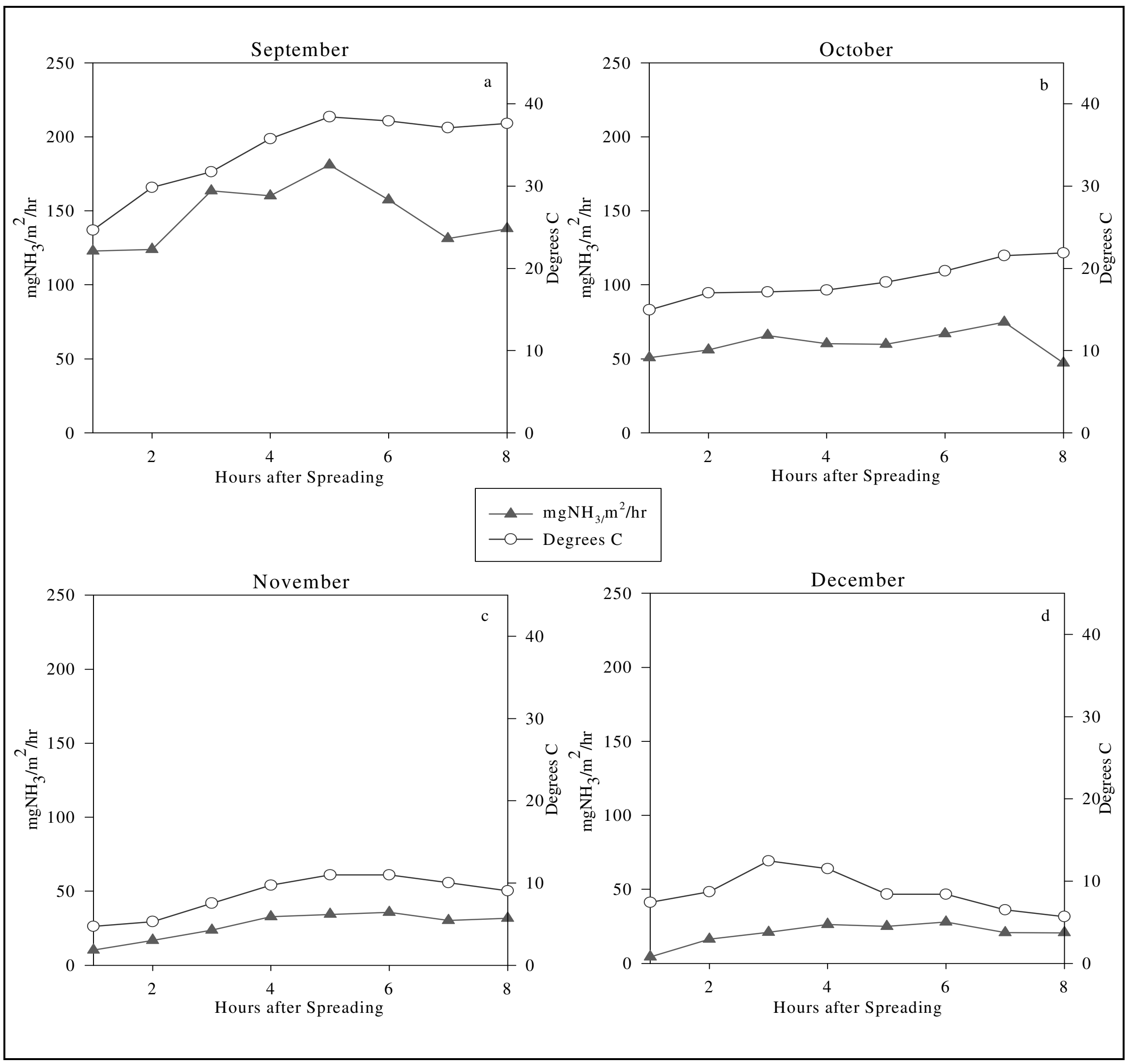


Figure 8. Ammonia volatility and temperature measurements in the first eight hours after spreading manure

Ammonia volatility from liquid dairy manure was significantly reduced in the first eight hours after surface application with increasingly cooler temperatures every month from

September – December (Figure 8), though the mean temperature in December was greater than the mean temperature in November. The correlation coefficient, r, relating hourly temperature averages in the chamber to rates of ammonia volatilization during the first eight hours after manure application is 0.93. This r value is significant at a probability (P) < 0.0001. The significance of temperature is primarily due to differences from month to month, not to differences in the temperature over the period of sampling within each month.

Manure of increasing nitrogen concentration was applied to experimental plots each month. Manure sample results identified that nutrient concentrations changed over a period of four months while remaining in the storage tank on the dairy farm (Table 4).

Table 4. Nutrient content of manure on a wet weight basis

Nutrient Content	**September**	**October**	**November**	**December**
% Total Nitrogen	0.25	0.30	0.34	0.34
% NH_4- Nitrogen	0.16	0.17	0.18	0.19
% Organic Nitrogen	0.09	0.13	0.16	0.15
% P_2O_5- Phosphorous	0.11	0.09	0.07	0.14
% K_2O- Potassium	0.38	0.38	0.24	0.34
Ppm Copper	7	7	12	7
Ppm Zinc	19	15	23	17
% H_2O	92.5	94.6	91.9	92.5

The causes for increasing concentrations of NH_4 in the manure from the storage tank are uncertain.

Focusing on the nitrogen content of the manure, it is evident that approximately half of the nitrogen content is in the form of ammonia at the time of application to the field (Figure 9). This is concordant with studies conducted by Jokela and Meisinger (2008) in which 30 random liquid manure samples from the state of Vermont were analyzed for TKN and ammoniacal-N content. When averaged, the manure contained 25 lbs total nitrogen per 1,000 gallons manure, and approximately half of that was in the form of ammoniacal nitrogen.

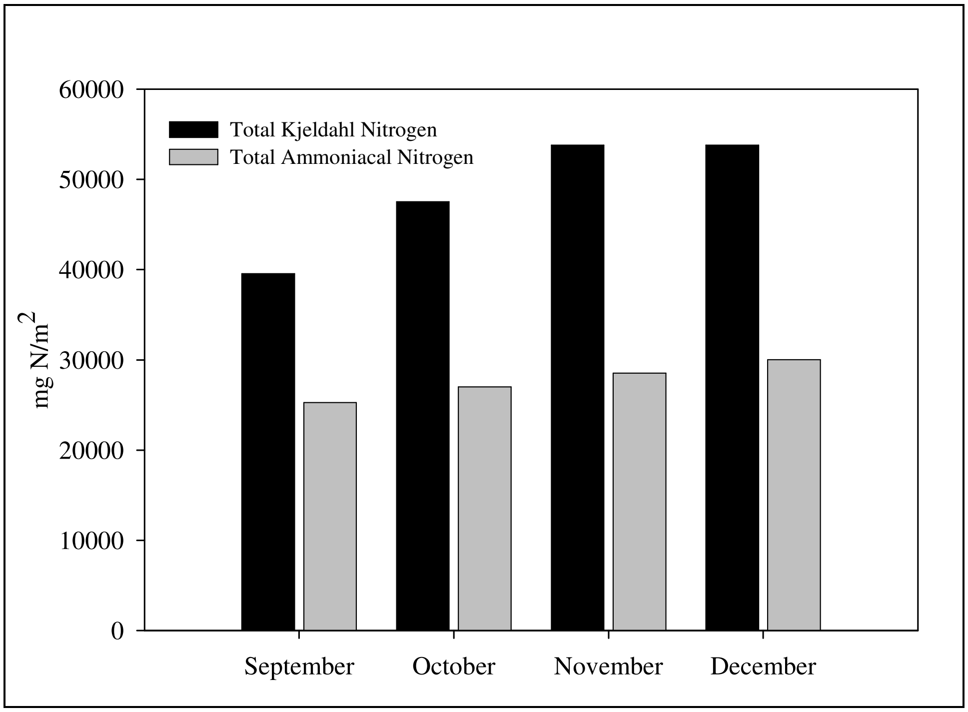


Figure 9. Total Kjeldahl nitrogen (TKN) applied vs. total ammoniacal nitrogen (TAN) applied each month

The ammoniacal portion of the manure applied to the field could be transformed by several pathways; volatilize as ammonia, undergo nitrification, be taken up by plants, or become immobilized by microbes. The organic N portion of the manure had to first decompose then undergo ammonification by the urease enzyme to be further transformed (Sylvia et al., 2005). These transformations of nitrogen contribute to the overall nitrogen cycled or lost. The fate of the fall applied nitrogen by springtime determined the efficiency of the spreading date for retaining nitrogen within the field if a cover crop is well established.

The secondary goals of this research addressed nitrogen retention from surface-applied manure. Soil NO_3 amounts in the spring are the portion of applied nitrogen that has undergone nitrification and is available for plant uptake. Surface application of manure in the late fall when air and soil temperatures have decreased reduces nitrogen loss due to nitrate leaching as well as to ammonia volatility. The cold temperatures reduced potential for N mineralization, nitrification, and ammonia volatilization. In a three year study conducted by Van Es et al. (2006) a late fall surface application of liquid dairy manure produced less leachate than an early fall application and produced amounts of leachate equal to spring applications of manure. In the same study, nitrate leaching from loamy sand was 2.5 times greater than from a clay loam. Many Massachusetts soils may be of greater risk to nitrate leaching than others due to the high sand content.

Changes in soil nitrate content measured over the period of this research are consistent with commonly accepted trends; as temperatures get colder less nitrate is present in the soil due to lack of activity from autotrophic nitrifiers. Days after spreading did not cause significant amounts of variation in soil nitrates at a depth of 0-15 cm in the months of December and November, however, had a highly significant ($P < 0.0001$) effect on variations in soil nitrates in the months of October and September (Figure 10). In soil samples taken from a depth of 15-30 cm the effect of day within month was not significant for the months of December, November, and October but was highly significant ($P < 0.0001$) for samples taken during the month of September (Figure 10). Nitrate concentrations are reported based on a soil bulk density of 1.3 g/cm^3.

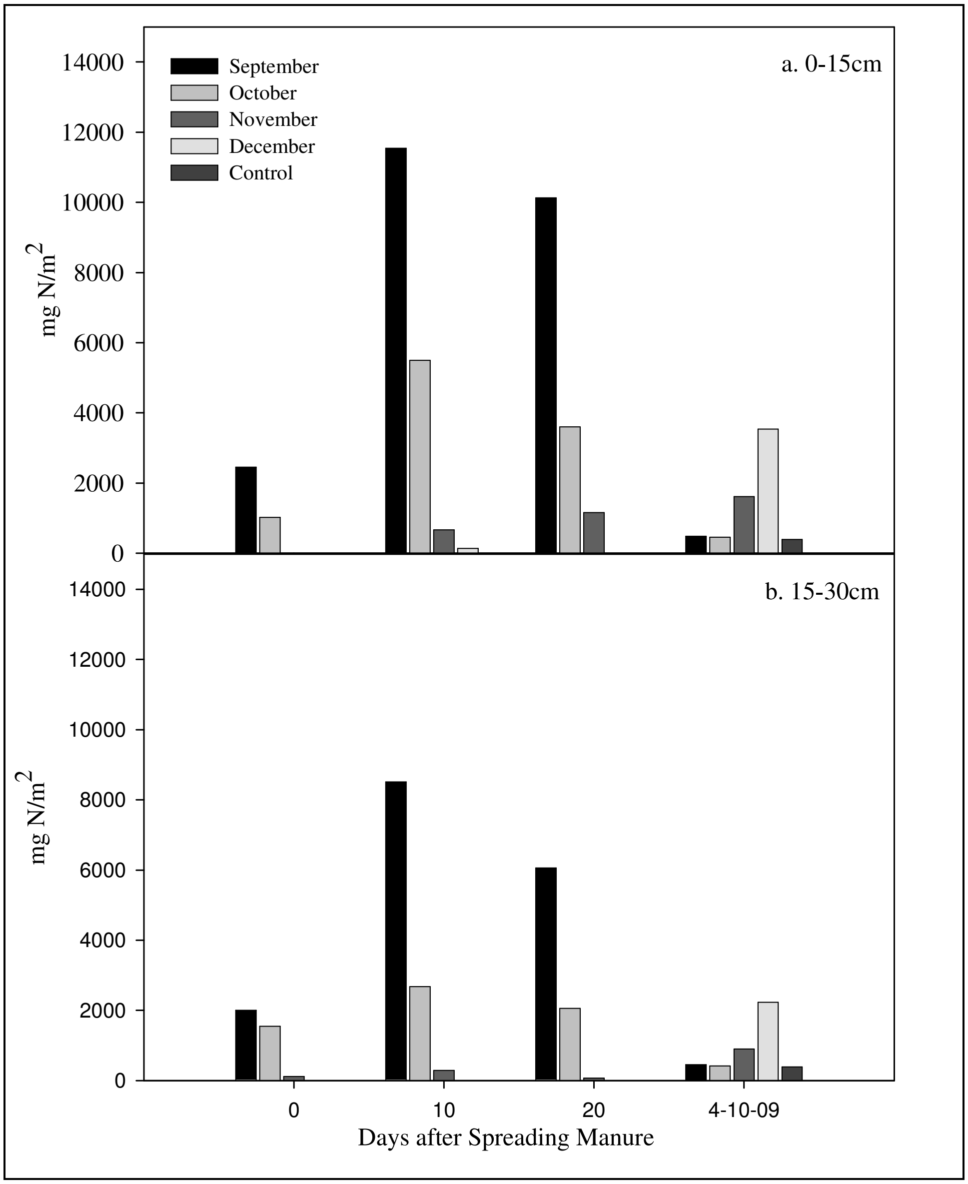


Figure 10. Soil NO_3-N concentrations September 2008–April 2009

September soil nitrate levels were highest in the fall, but were second lowest in the spring with comparable quantities of nitrate to the control plot which received no manure indicating that almost all the nitrogen applied in September of 2008 had leached, volatilized, or was in plant tissue by the spring of 2009. October soil nitrate concentrations were second highest during the fall, and were similar to the September and control plots' spring nitrate concentrations. All plots contained greater concentrations of nitrate in the upper portion of the soil (0-15 cm) (Fig 10a) than the lower portion (15-30 cm) (Fig 10b) except in the month of October before manure was spread. Rainfall in October may have caused nitrates to leach deeper into the soil profile resulting in less nitrate measured in the spring also.

Greater nitrogen retention in soils below plots spread with manure in November and December may be due to the inactivity of nitrifying bacteria in colder temperatures or due to the fact that they have less time to leach than September and October applications. Nitrogen content of manure which has quickly undergone ammonification could be stored over winter in the form of ammonia in the soil, and be nitrified as temperatures warm up in the spring. Nitrogen from a September application of manure could be oxidized during the fall while temperatures are still warm and leached as nitrates rather than retained for crop use in the spring.

Tissue samples analyzed for Total Kjeldahl Nitrogen from each treatment plot were sampled on October 30, 2008; November 30, 2008; December 30, 2008; and April 10, 2009. Amounts of mg N/m^2 varied with each month of sampling as well as between treatment plots partially due to the varied growth of cover crop tissue, and partially due to seasonal rates of nitrogen uptake by *Secale cereale* L. (Figure 11). TKN mg N/m^2 in the September plots increased between November 30 and December 30, 2008 apparently due to cover crop growth during this period.

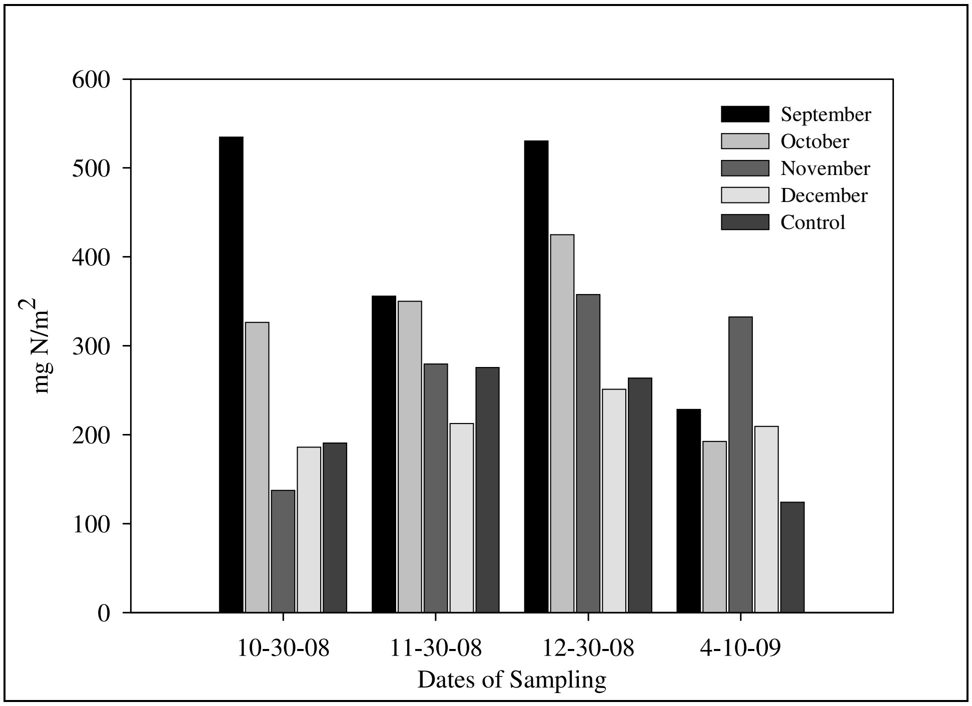


Figure 11. TKN in *Secale cereale* L. sampled from each treatment plot on different dates

Tissue total nitrogen contributions to the field in April, were varied with rye growing on the November plots retaining the greatest amount of nitrogen from the manure application, September retaining the next greatest amount and October and December having fairly similar retention rates. Tissues sampled from all plots contained higher amounts of TKN at the end of the month after spreading manure than in the spring. Overall, the amount of TKN in the cover crop leafy tissue is much less than nitrate nitrogen in the soil. The cover crop planting may not have been well enough established to retain a significant amount of nitrogen for spring. Tissue samples were also not representative of the plots therefore changes in mgN/m^2 from month to month are not a reliable account of the total nitrogen present in those plots.

A nitrogen retention rate was calculated for the nitrogen applied from manure in the fall of 2008 by using amounts of nitrates in the soil and TKN in the tissue to calculate retained N of samples taken in the spring of 2009. Percent N retention can be calculated by the following equation:

$$\%R = 100\times(NS + NT)/NA$$

where %R is percent nitrogen retained, NS is the soil nitrate-N in mg N/m^2 to a depth of 30cm, NT is tissue TKN in mg N/m^2, and NA is total nitrogen applied in the form of manure. Percent retention of nitrogen applied (NA) were 5%, 4%, 10%, and 22% from manure applied in September, October, November, and December 2008 respectively.

Retained nitrogen in the spring in the form of soil nitrate and cover crop tissue TKN from fall application of manure can be compared to ammoniacal nitrogen losses measured each month to gain an understanding of nitrogen use efficiency (Figure 12).

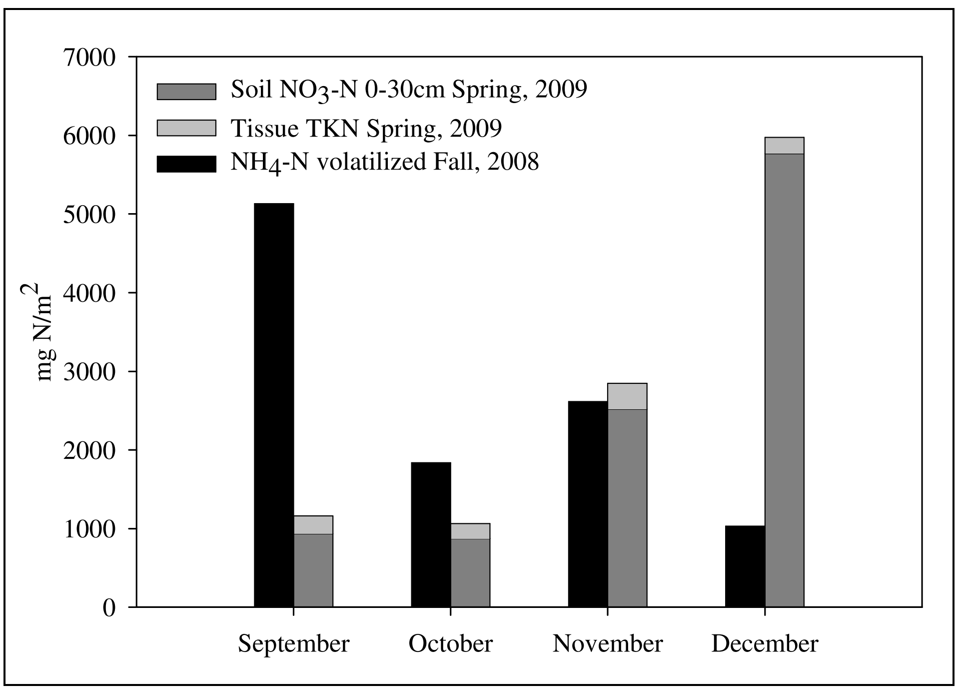


Figure 12. Nitrogen efficiency based on NH_4-N losses vs. soil NO_3-N and tissue TKN retention each treatment month

Surface-applied manure spread in September had the greatest rate of volatility and the least amount of nitrogen retained for crop growth in the spring making this the least efficient manure spreading time. Surface-applied manure in December had the least amount of volatile ammonia losses, while retaining the greatest amount of nitrogen for use by crops making this surface application the best choice for nitrogen retention from the manure regardless of frozen ground. The November manure application resulted in an almost 1:1 ratio of ammonia lost to nitrogen retained, and although more ammonia volatilized this month than in October, more nitrogen was also retained. Rains in October were likely the reason that ammonia volatility was less than in November, and much of the available nitrogen was likely leached due to slowed cover crop growth at this time of year, resulting in low soil nitrate retention in the spring 2009 (even less retention than from September's manure application).

However conclusive the results discussed above may be, a large portion of the total applied nitrogen in the fall of 2008 was unaccounted for; it was not measured as lost *or* retained in the spring of 2009. This unaccounted nitrogen is considered as 'potential loss' and can be calculated as:

$$PL = NA - NL - NT - NS$$

where PL is potential loss, and all other units and coefficients are as mentioned in the equations for percent nitrogen lost and retained above. Figure 13 shows total values for NA (including organic-N and ammoniacal-N portions) compared with NL, NT, and NS from each treatment plot.

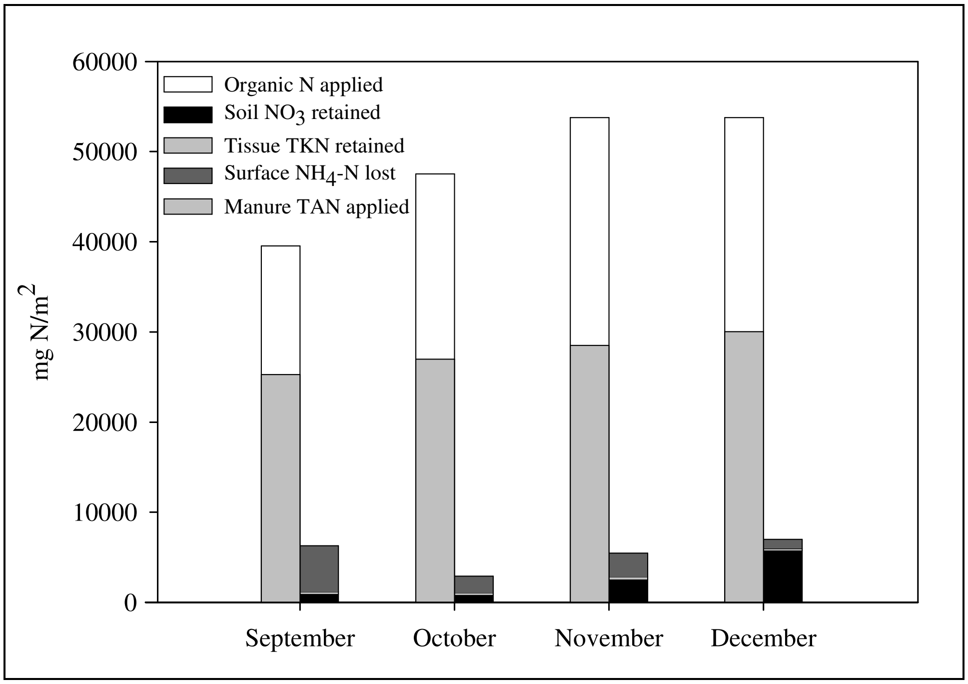


Figure 13. Total nitrogen applied vs. all other nitrogen measurements

Potential losses in order of greatest to least are: November, October, December, and September. Most of the retained nitrogen in the form of tissue TKN and soil NO_3 from the December application are likely from the total ammoniacal portion of the manure, while the retained portion of nitrogen from the September application may come partially from decomposed organic-N. Future research on ammonia volatility and nitrogen cycling from surface-applied manure must make attempts to account for the potential losses identified above by sampling a larger variety of potential nitrogen sinks such as leachate or cation exchange sites in the soil.

Conclusion

Notice how many times I have said "manure?" It is serious business.
It breaks the farmers' backs. It makes their land.
It links the eternal, binding man and beast and earth.

-Hayden Carruth

Manure management is focused around maintaining the nitrogen within a farm system without losing any to the atmosphere or ground water; in a sense, completing the nitrogen cycle "links the eternal". Reduction of ammonia volatility is one step of manure management for nitrogen retention that is only effective if that nitrogen is cycled through the farm system and not lost by other pathways such as nitrate leaching. To summarize the findings from this research: largest ammonia volatility rates, soil nitrate levels, and cover crop TKN amounts occurred in the fall of 2008 on plots applied with manure in September. Colder temperatures significantly reduced rates of volatility and amounts of nitrate found in the soil. However, N-uptake by plants during the fall fluctuated and was not significantly different from month to month. Plots applied with manure in October had the least amount of retained nitrogen in spring 2009 measurements (Figure 12). November plots retained the greatest cover crop tissue TKN in the spring of 2009 (Figure 11). December plots had the greatest soil nitrate retention in the spring (Figure 10) despite application of manure to frozen ground.

Despite current Massachusetts Department of Agriculture Best Management Practices (2009) that strongly discourage the application of manure to frozen ground, the results from this research conclude that the greatest nitrogen retention came from manure applied to frozen ground in December. The coldest temperatures and least amount of ammonia losses were measured this month also. These findings should not be accepted as a best management practice without further investigation of other nitrogen transformations, but they do suggest that current recommended practices may need to be challenged. This research only partially addressed the issue of the fate of nitrogen related to surface-applied manure in the fall. The fate of a majority of the nitrogen applied at cooler fall temperatures is still uncertain. Although ammonia volatility rates fall below detection levels, the volatility may continue to occur over a long period of time so that overall amounts of ammonia loss from manure applied in December may be close or equal to losses from manure applied in September. Surface runoff or nitrate leaching could also be significant sources of nitrogen loss from surface-applied manure. However, simply based on the analysis made in this research, surface application of liquid dairy manure should be conducted as late as possible in the fall before snow fall for the greatest retention of nitrogen for crops in the spring. Planting a cover crop at the time of harvest in conjunction with a late fall (November or December) manure application is a nutrient management strategy which deserves further investigation.

Research conducted in the future on ammonia volatility from surface-applied manure should include some or all of the following suggestions in order to obtain more complete results:

1) Measure ammonia volatility for longer periods of time until levels are no longer detectible.

2) Samples should be taken at the same time in relation to time of spreading each month so that results are comparable at all sampling times rather than just the first eight hours as was the case in this research.

3) Manure application and ammonia sampling should be conducted at rates similar to a farmer’s field application rate in order to obtain more realistic data.

4) Wind speed, rainfall, soil moisture, and soil pH should all be measured to better understand environmental effects on ammonia volatility. Consequently, modeling of ammonia volatility under the above mentioned environmental factors could be used to predict changes in volatility rates, depending on these ambient conditions.

5) Soils should be analyzed for ammonia content to see if ammonia nitrogen is being stored on cation exchange sites in the soil throughout the period of the experiment.

6) Manure samples could be taken periodically at the same time soil samples were taken and analyzed for TKN to monitor amounts of total nitrogen left in the manure over time.

Other experiments that can be conducted using fairly similar methods as those used in this research and which would provide some missing and valuable information are:

1) Surface application of manure to fields which have been planted with a cover crop on different dates to see if nitrogen retention rates change or could be improved.

2) Monitor ammonia emissions from pastures spread and injected with manure to provide useful information to the increasing number of dairy farmers grazing their animals and unable to incorporate manure into their pastures.

APPENDIX A

NITROGEN CYCLE

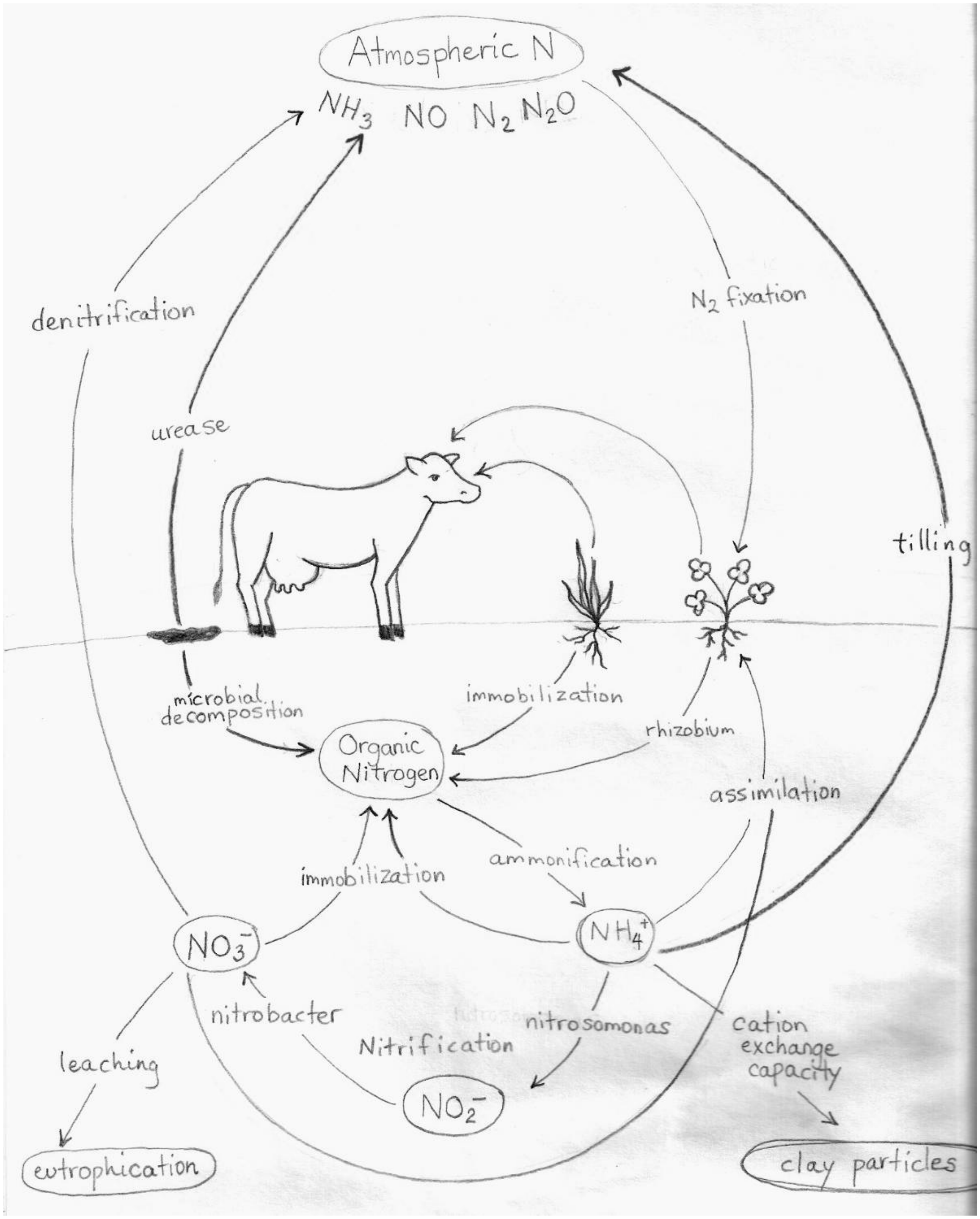


Figure A-1. Author's interpretation of the Nitrogen Cycle based on: Sylvia, D.M., Fuhrmann, J. J, Hartel, P.G., and Zuberer, D. A. (2005). *Principles and Applications of Soil Microbiology, 2nd ed.* New Jersey: Pearson Education Inc.

APPENDIX B

MANURE SOURCE: MT. TOBY FARM, SUNDERLAND, MA

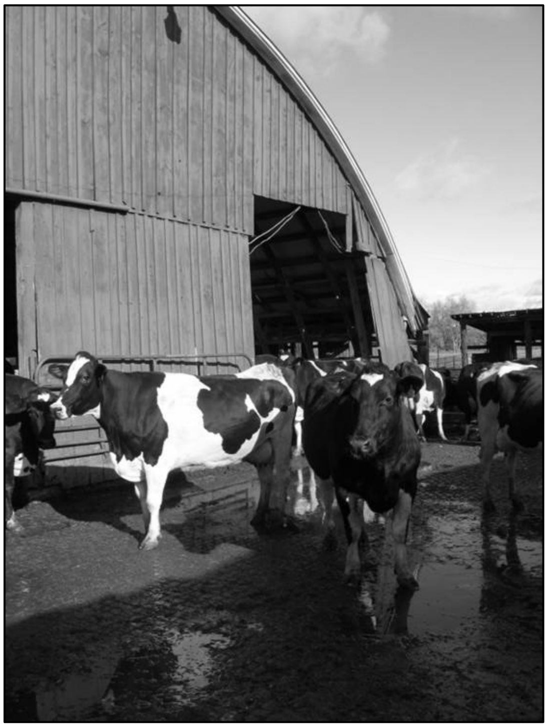


Figure B-1. Dairy cows and barnyard floor showing effluent (manure, feces, and water)

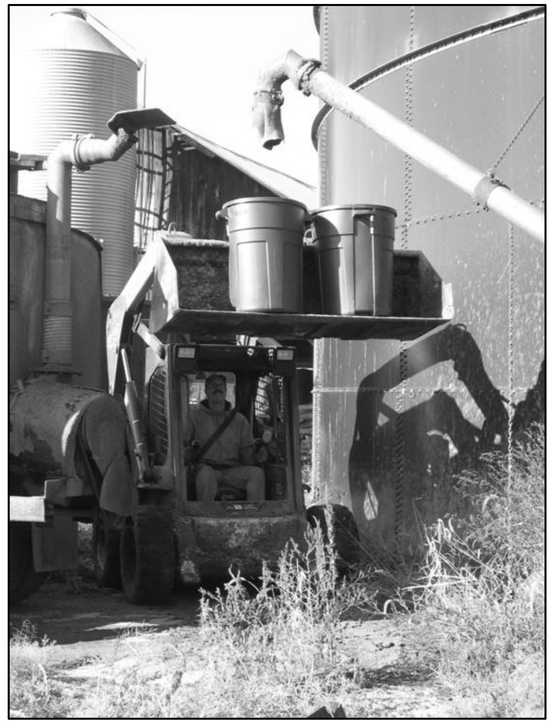


Figure B-2. Collecting manure for application in field experiments

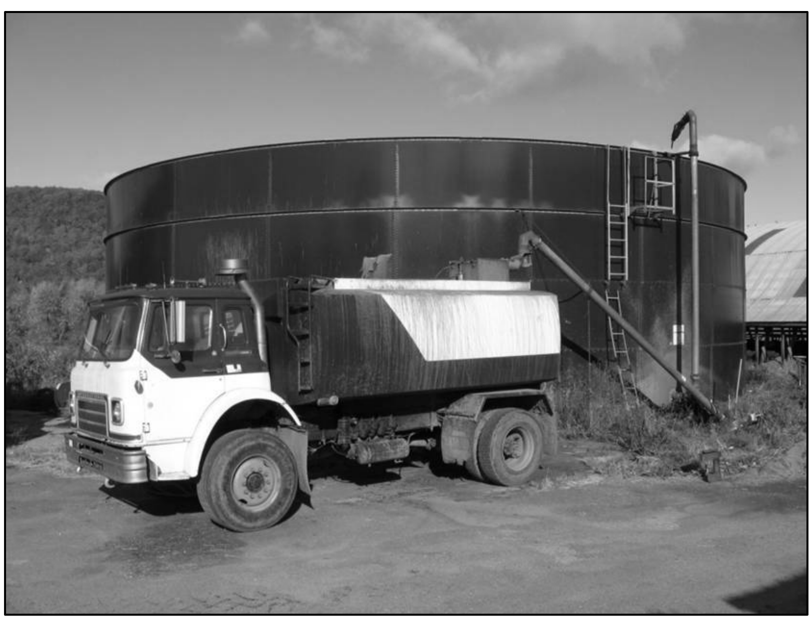


Figure B-3. Manure storage tank and manure spreader with 2,000 gallon carrying capacity

APPENDIX C

APPLICATION OF MANURE AND SAMPLING AMMONIA VOLATILITY

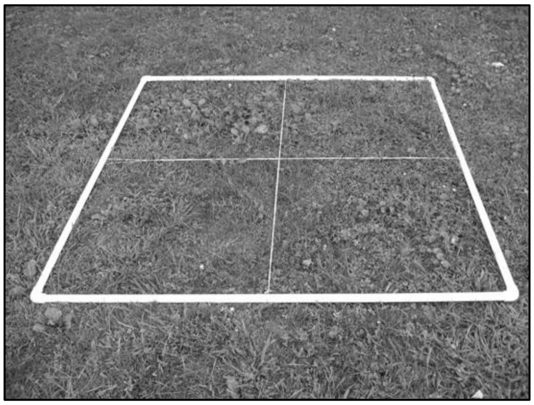


Figure C-1. The 1.5m by 1.5m square made of 1.75cm PVC pipe was divided with string into $4m^2$ sections.

Figure C-2. 3.26 liter of manure was poured in the center of each section using a gallon milk jug.

Figure C-3. One ammonia volatility chamber in a plot during a one-hour sampling period in September 2008

Figure C-4. Several ammonia volatility chambers during a one-hour sampling period in November 2008

Figure C-5. Ammonia volatility chamber after one hour of sampling

Figure C-6. Sampling jars ready for transport back to the lab

APPENDIX D

OCTOBER 2008 FIELD DATA SHEET

Run Title: October Manure

Location: CAREC Block 18

Notes: Ground harder this month, so chambers do not seal well to the ground

Date	Plot #	Sample#	Time IN	Time OUT	°C at OUT	Hrs After Spreading / Notes
10/2/08	B3	84	8:20 am	9:20 am	14.9	1 All jars in Shade
	C3	76	8:20 am	9:20 "	15.2	1 "
	B2	68	8:25 am	9:25 "	15.0	1 "
	D2	60	8:25 am	9:25 "	14.6	1 "
	D1	52	8:30 am	9:30 "	15.6	1 (some sun) "
	E1	43	8:30 am	9:30 "	14.6	1 (some sun) "
	Ambient Air			9:20 "	15.0	
	B3	83	9:20 am	10:20 "	15.8	2 Cloudy & cool
	C3	73	9:20 "	10:20 "	15.7	2 "
	B2	67	9:25 "	10:25 "	16.0	2 "
	D2	59	9:25 "	10:25 "	15.7	2 "
	D1	51	9:30 "	10:30 "	15.9	2 "
	E1	44	9:30 "	10:30 "	15.5	2 "
	Ambient Air			10:30	14.4	
	B3	82	10:20 am	11:20 am	17.8	3 Sun at last!
	C3	74	10:20 "	11:20 "	18.5	3
	B2	66	10:25 "	11:25 "	17.5	3
	D2	58	10:25 "	11:25 "	17.3	3
	D1	50	10:30 "	11:30 "	17.1	3
	E1	42	10:30 "	11:30 "	16.8	3
	Ambient Air			11:30	14.4	
	B3	81	11:20	12:20 pm	17.1	4 fan on ground/fan fell, acid spilled
	C3	75	11:20	12:20 pm	17.2	4
	B2	65	11:25	12:25 pm	17.1	4
	D2	57	11:25	12:25 pm	16.9	4
	D1	49	11:30	12:30 pm	17.1	4
	E1	41	11:30	12:30 pm	16.9	4
	Ambient Air				15.6	
	B3	80	12:20 pm	1:20 pm	17.3	5
	C3	72	12:20 pm	1:20 pm	17.6	5
	B2	64	12:25 "	1:25 "	17.5	5
	D2	56	12:25 "	1:25 "	17.3	5
	D1	48	12:30 "	1:30 "	17.4	5
	E1	40	12:30 "	1:30 "	17.3	5

Ambient Air → 16.3

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